ES 175
Progress in Electrolyte R&D within ABR Program: 2009~2013

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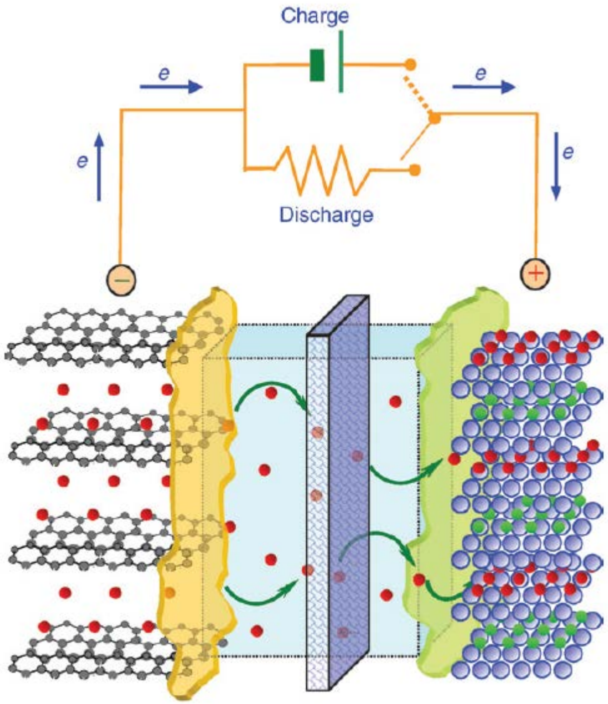
Challenges and Opportunities for Electrolytes

US ARMY RDECOM | ARL

Baseline Electrolyte: $LiPF_6$ in Carbonates (EC, DMC etc)

Electrolytes for Li Ion Battery (LIB)

- Higher Power Density
    - better SEI on anode
- Higher Energy Density
    - anodic stability on cathode
    - SEI on alloy/conv.-rexn. chemistries
- Service temperature
    - High temperature stability: automotive
    - Low temperature: space, military
- Safety:
    - overcharge Protection
    - non-flammability



Electrolytes for Beyond Li Ion (BLI) Chemistries

- Non-Carbonate
- Solid Polymer
- Ceramics
- Li Metal Protection
- Ionic Liquid

- Li/O_2
- Li/S
- Li/H_2O
- Na Ion
- Mg Ion

USABC Requirements For LIB Electrolytes

Parameters	SOA	Desired
Ion Conductivity	> 5 mS/cm (25 ^{o}C) > 1 mS/cm (-30 ^{o}C)	> 2 mS/cm (-30 ^{o}C)
Electronic Conductivity	<10^{-6} S/cm	
Li^{+} Transference Number	> 0.35	
Stability at Cathode	> 4.5 V vs. Li^{0}	> 5.0 V vs. Li^{0}
Viscosity	< 5 cP (25 ^{o}C) < 50 cP (-30 ^{o}C)	< 20 cP (-30 ^{o}C)
H_2O	< 20 ppm	< 5 ppm
HF	< 50 ppm	< 10 ppm
Vapor Pressure	< 20 mHg	< 1 mmHg
Flash Point	> 60 ^{o}C	> 100 ^{o}C
Cost	< $15/Kg	< $10/Kg

Electrolyte Efforts at DOE

Electrolyte Projects within ABR/BATT (11)

- Argonne National Lab (ANL)
- Arizona State University (ASU)
- Army Research Lab (ARL)
- Case Western Reserve University (CWRU)
- Idaho National Lab (INL)
- Jet Propulsion Lab (JPL)
- Lawrence Berkeley National Lab (LBNL)
- North Carolina State University (NCSU)
- Oak Ridge National Lab (ORNL)
- University of Rhode Island (URI)
- University of Texas-Austin (UTA)
- University of Utah

Research Foci

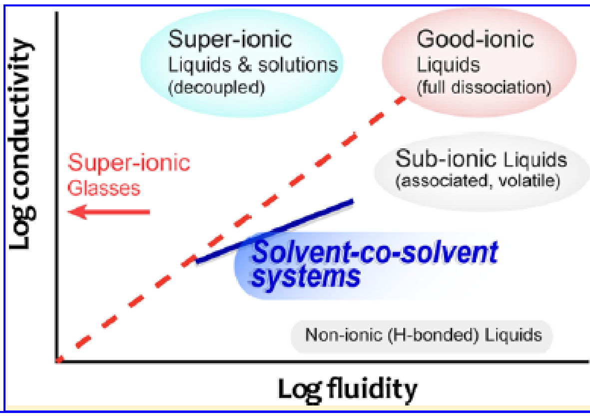
- Fundamental Understanding
  - SEI Additives
  - High Voltage Electrolytes
  - Overcharge Protection
  - Low Temperature Improvement
  - Solid Polymer
  - Ionic Liquid
  - Electrolytes for BLI Chemistries
- Simulations
- Materials Engineering

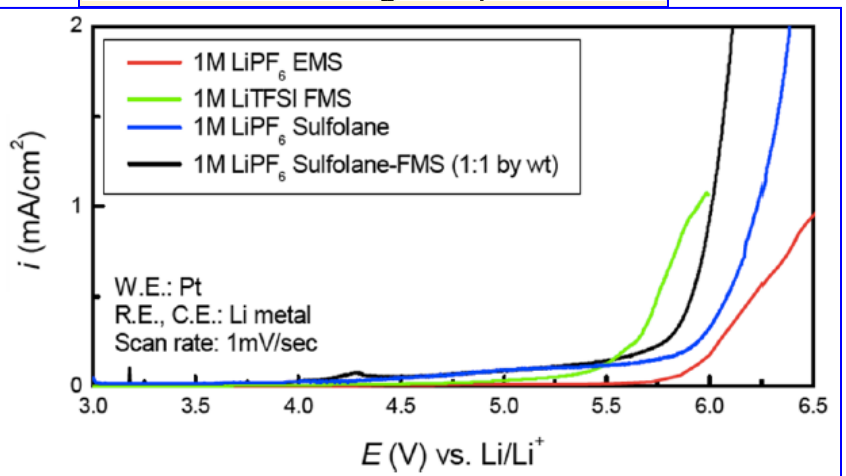
What differentiates ABR efforts from "other" electrolyte researches

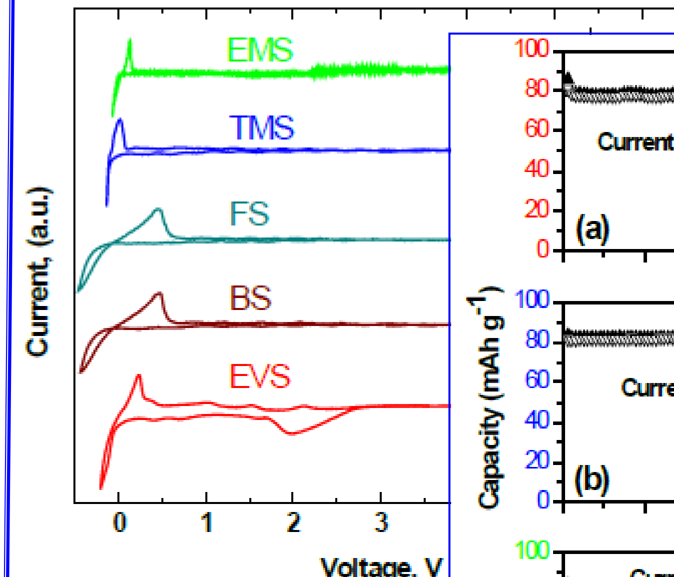
- Application-oriented
- Core facilities at National Labs
- Program-wide Standardized Tests

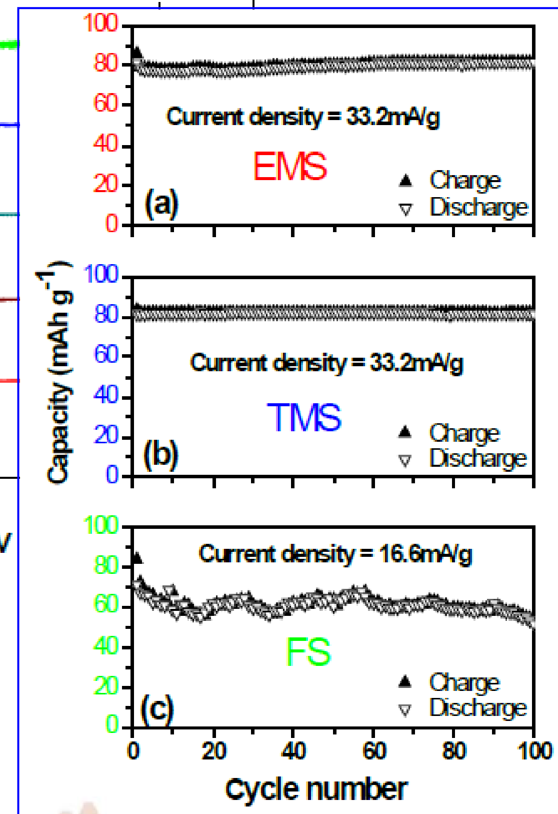
Sulfone-based Electrolytes

- **Advantage: exceptional anodic stability on cathodes**
- **Disadvantage: reduction at anode; high viscosity**









Arizona State Univ.
PI: Angell

Argonne Nat'l Lab
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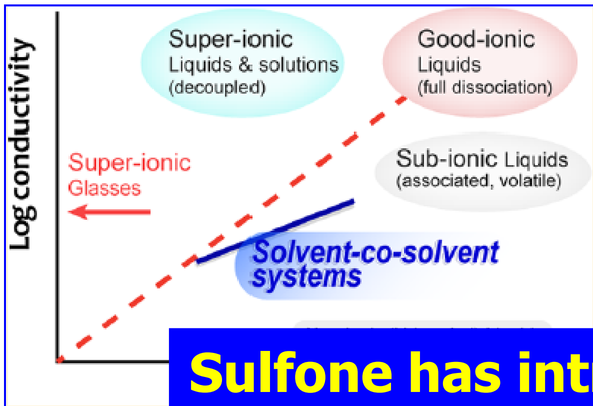

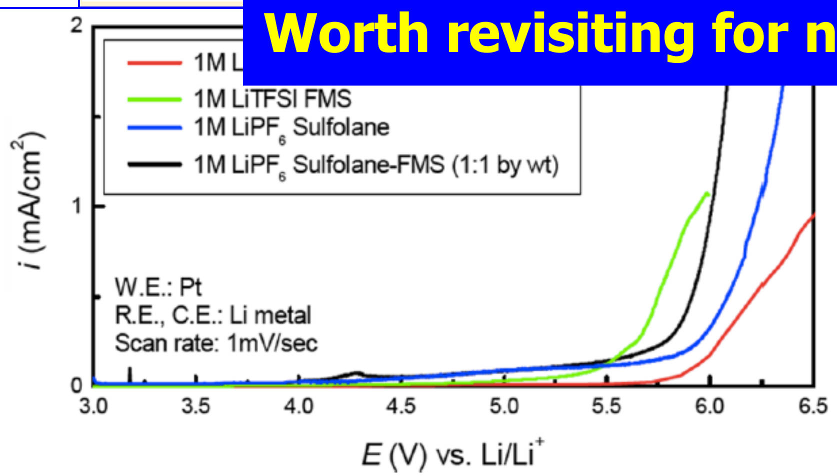

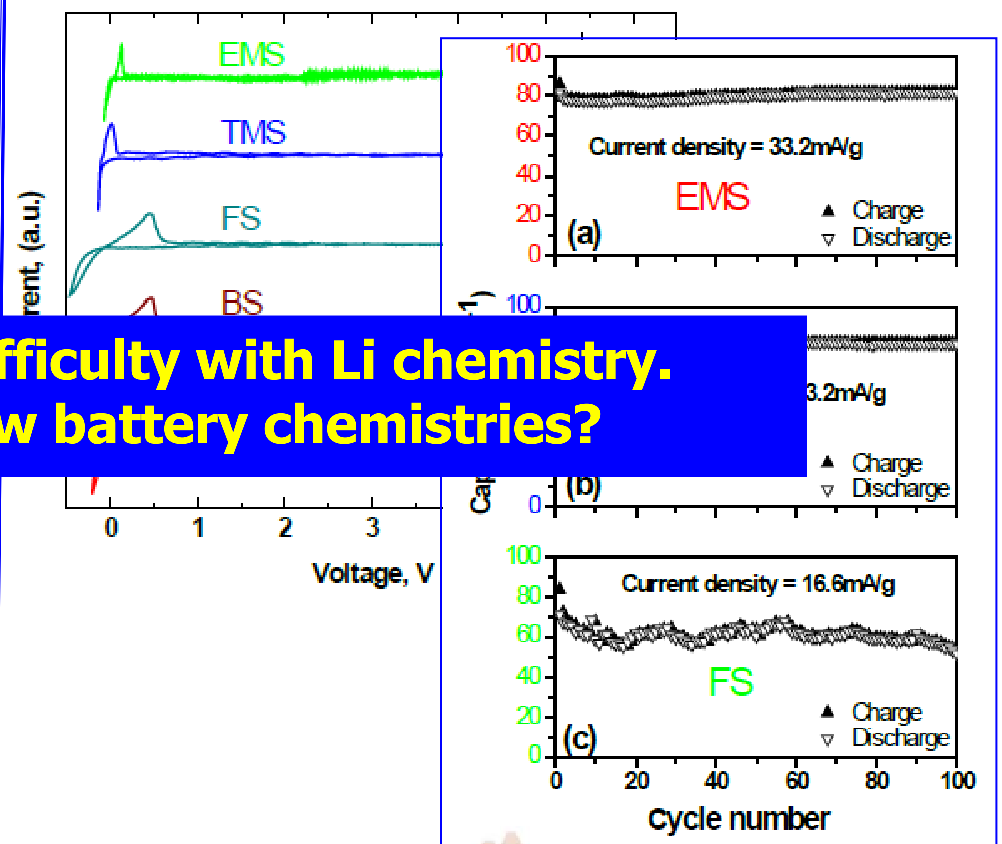

Sulfone has intrinsic difficulty with Li chemistry. Worth revisiting for new battery chemistries?

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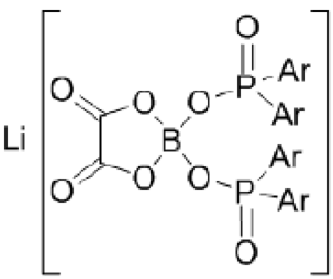
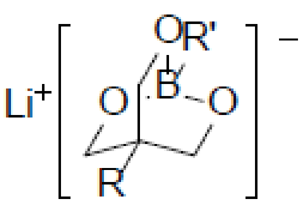
Bifunctional Salt Anion: FRION

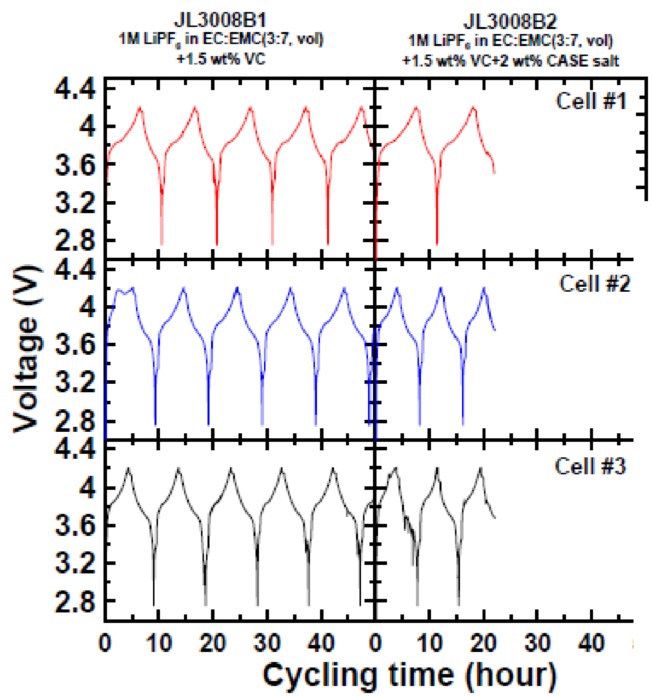
Functionalize anions of new Li salt

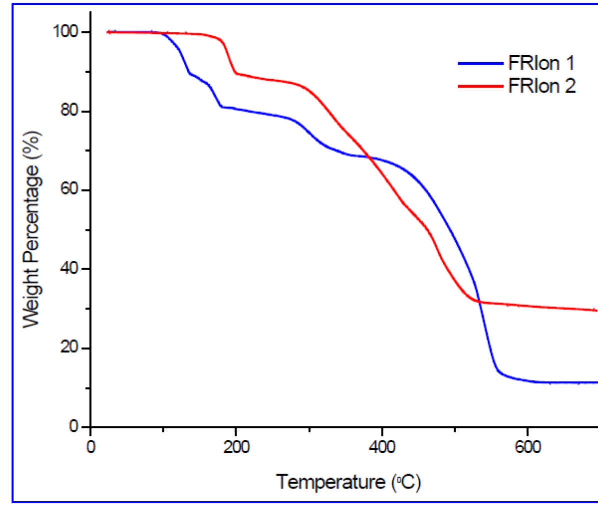
- flame retardation
- overcharge protection
- chemical stability
- thermal stability

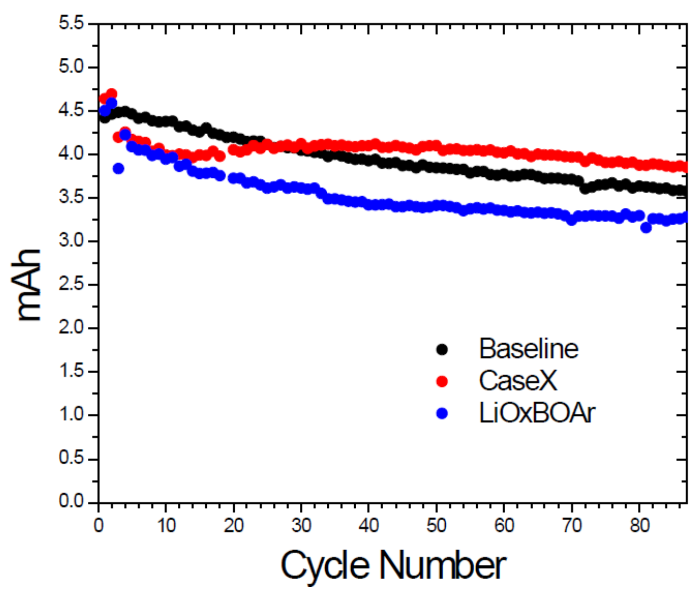




$LiC_RB_{R'}$







Case Western Reserve
PI: Scherson

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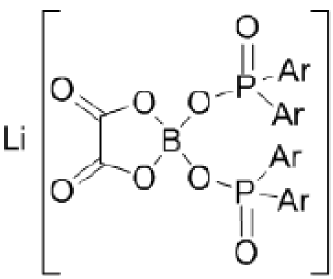
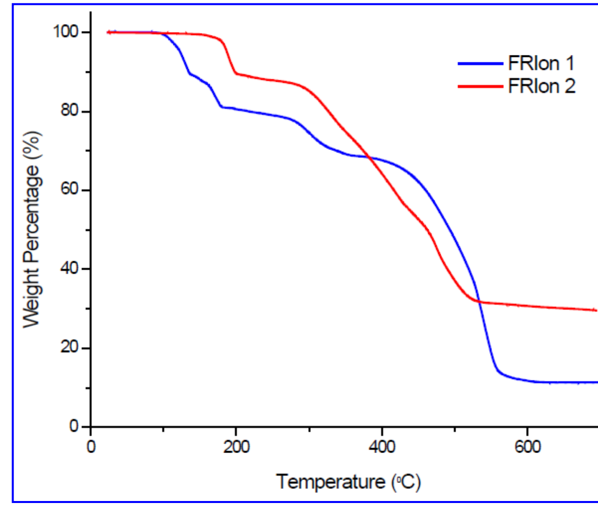
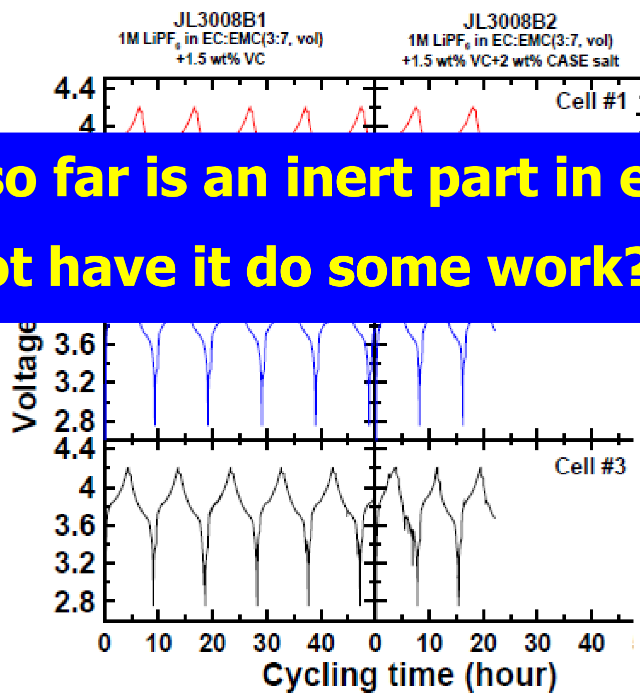
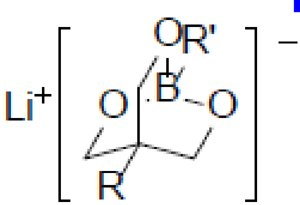




Anion so far is an inert part in electrolyte.

Why not have it do some work?





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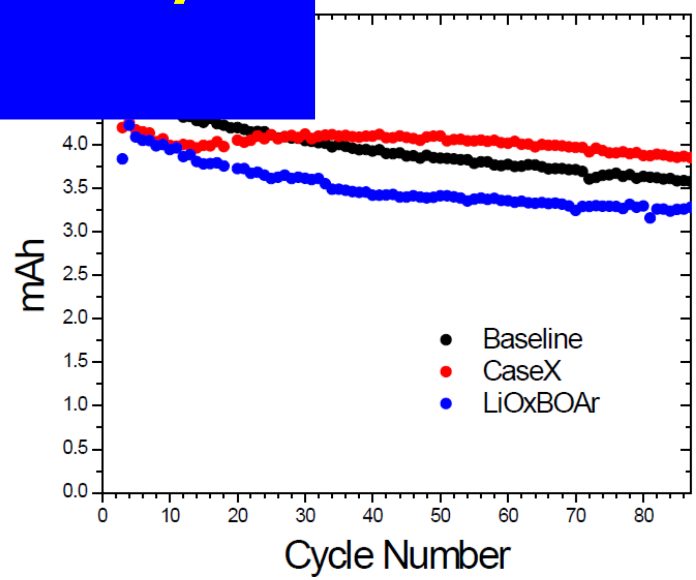

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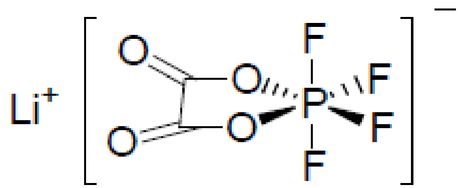
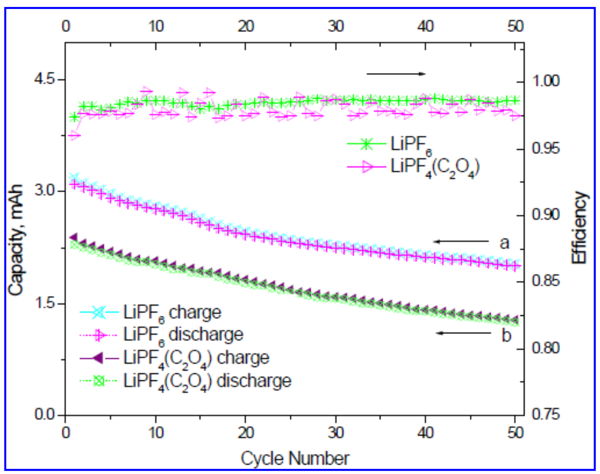
New Electrolyte Components

Functionalized new Li salt anion

- oxalato-substructure incorporated with PF_6^-
- higher thermal stability than PF_6^-
- positive effect on cell

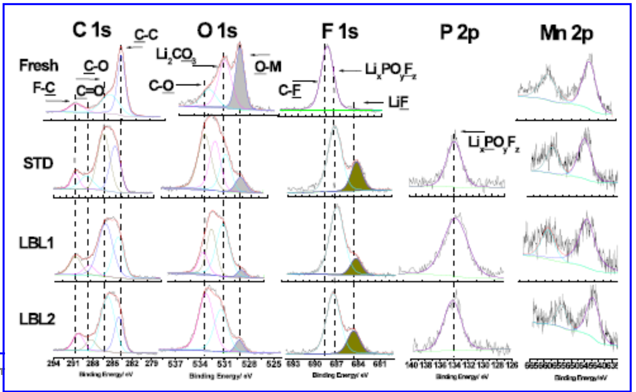


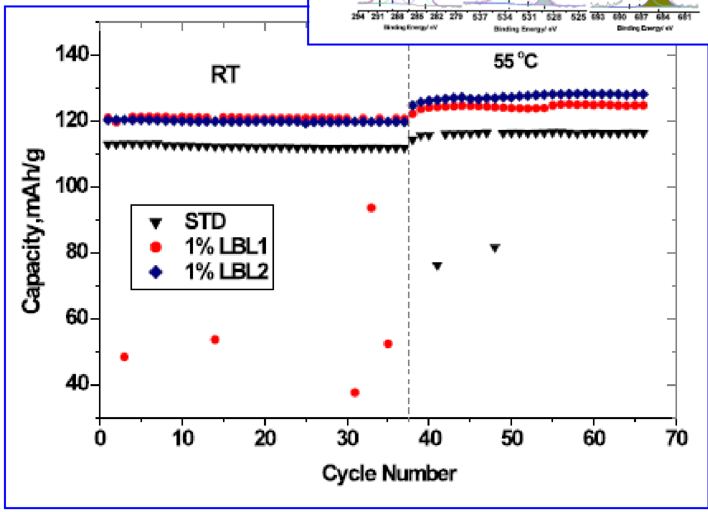


Additives for Cathode-film

BOB or Lewis base as electrolyte additives

- new interphase retains Mn better
- positive effect on half-cell at HT





Univ. of Rhode Island
PI: Lucht

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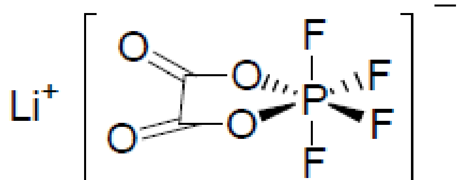

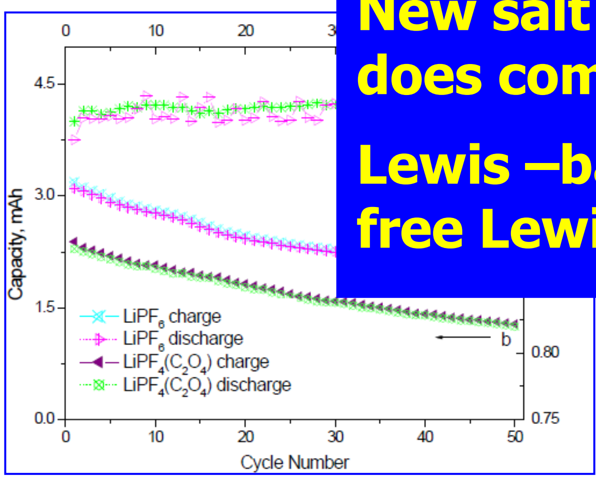

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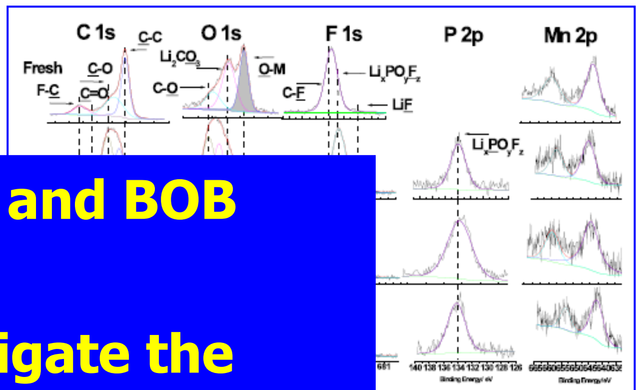
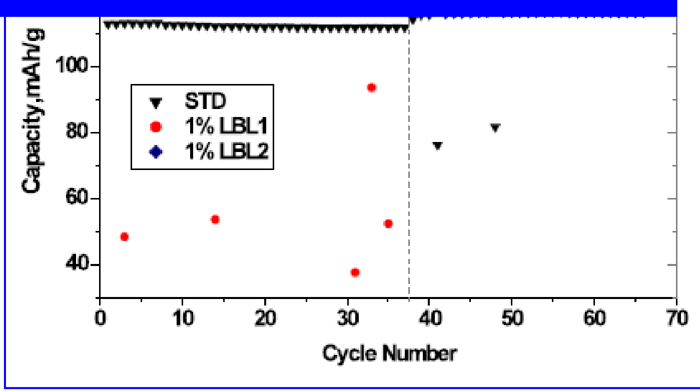


New salt anion as hybrid of PF_6 and BOB does combine benefits of both.

Lewis –base additive might mitigate the free Lewis acid PF_5 in electrolyte.



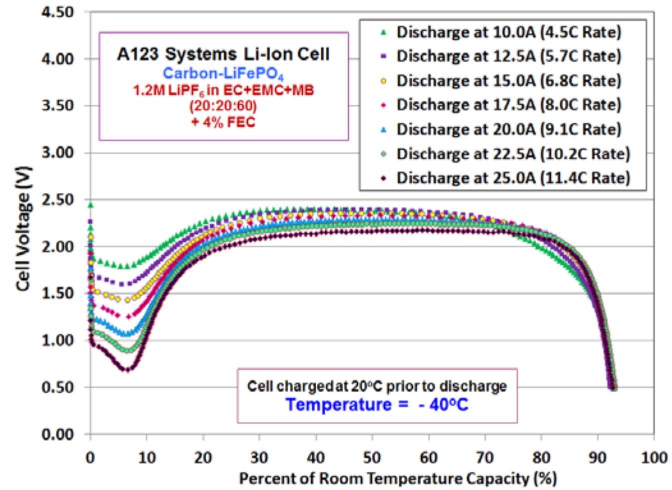
Univ. of Rhode Island
PI: Lucht

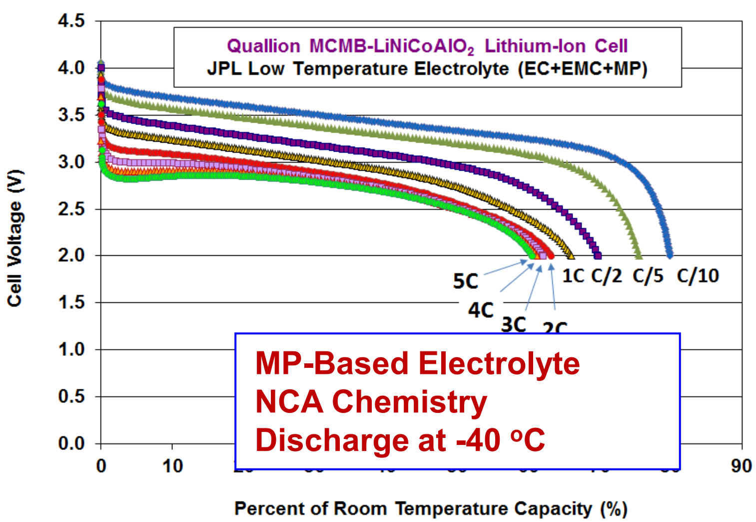
TER FOCUSED.

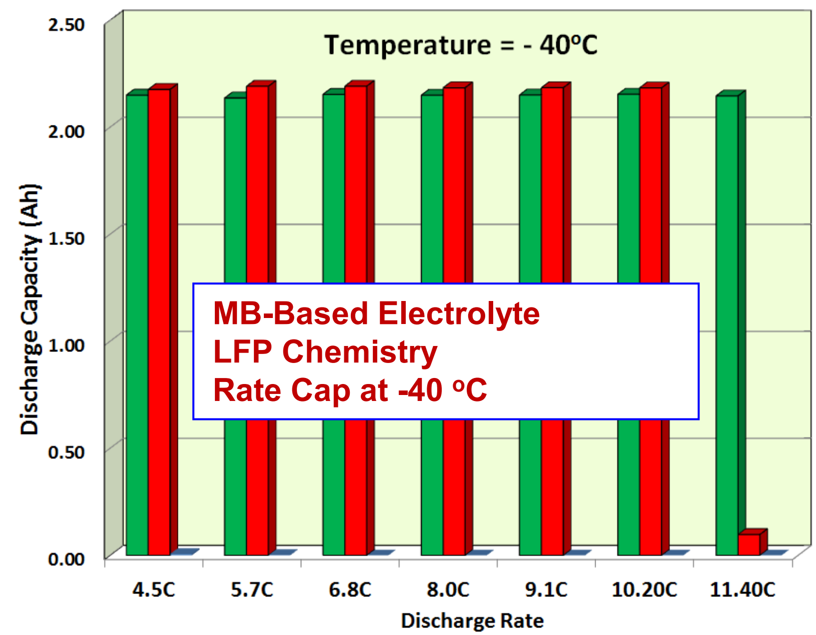
Low Temperature Electrolytes

A Different Perspective from NASA

- Space mission requires energy-delivery at extra-low temperatures
    - -40~-60 ºC
- Approaches:
    - incorporation of carboxylic esters
    - restricted use of EC
- Challenges: maintain cycling stability at HT





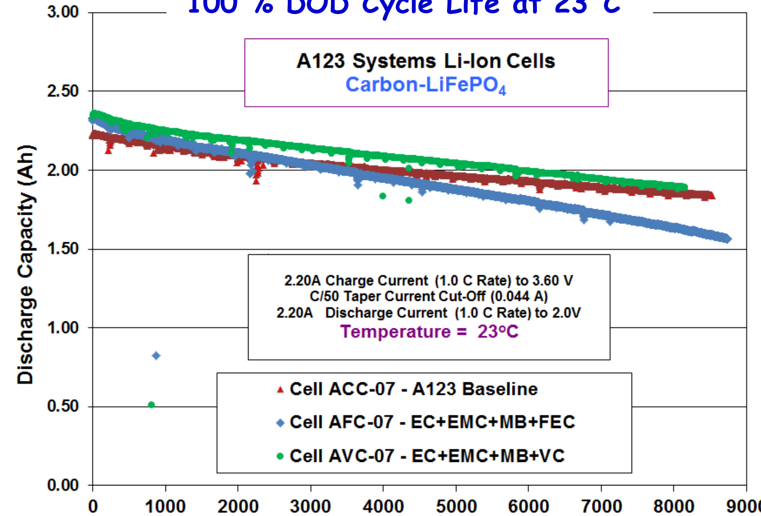


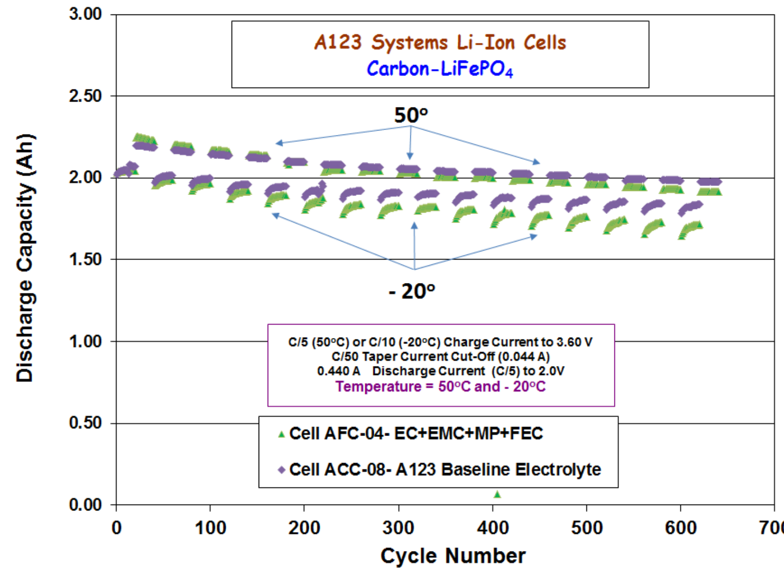
Jet Propulsion Lab
PI: Smart

Low Temperature Electrolytes

- Cycle-life not impacted by these carboxylates
  - Impressive life characteristics are observed at 23oC, with ~ 8,000 cycles being demonstrated (100 % DOD cycling). The methyl butyrate-based electrolytes delivers comparable performance to the baseline electrolyte (> 81% of the initial capacity after completing 8,000 cycles).
- HT (50 oC) stability
  - Cells containing the JPL developed electrolytes demonstrate good preservation of the low temperature capability after being subjected to high temperature (i.e., +50°C).

100 % DOD Cycle Life at 23°C





Discharge Rate Capability at -40°C

JPL

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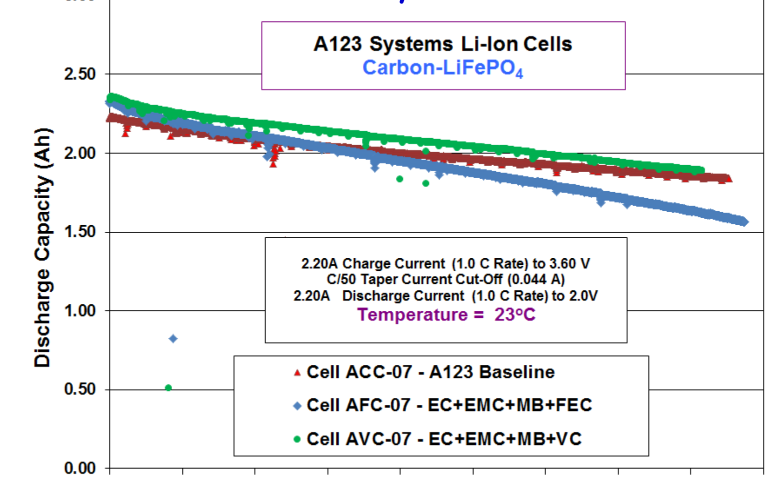
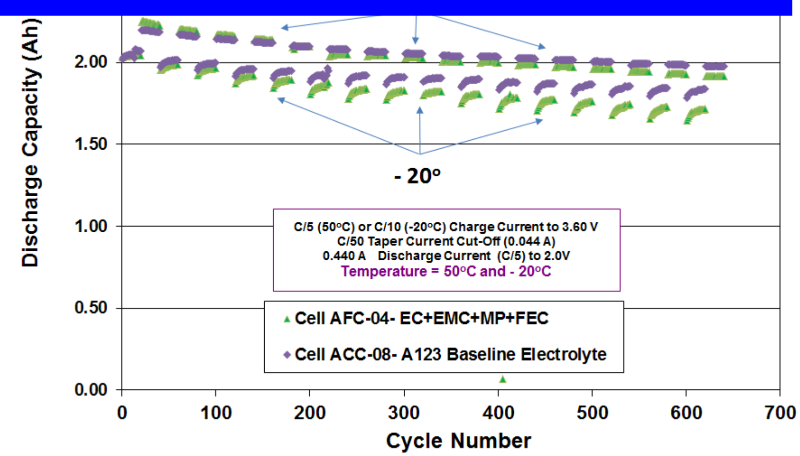


Carboxylate addition clearly improves LT rate capability. Compromise in HT performance mitigated



Discharge Rate Capability at -40°C

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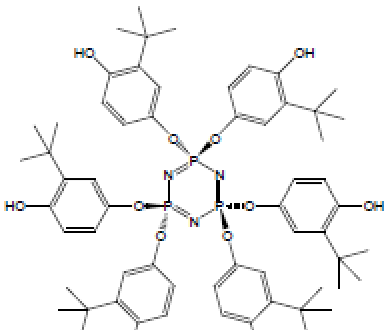
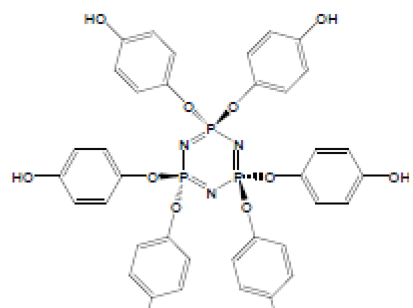
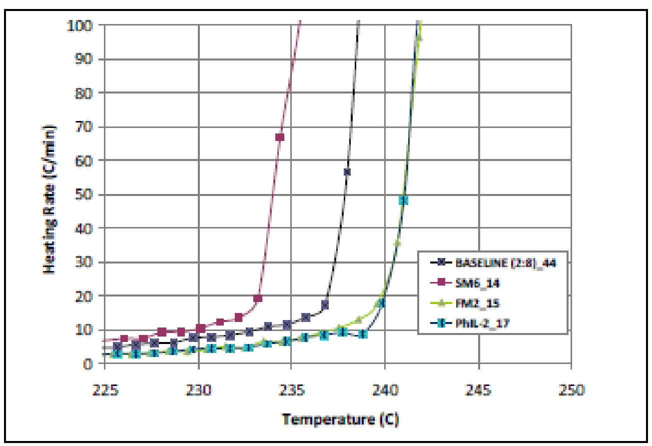
Functionalized Phosphazenes

- 1980s: Polyphosphazenes with EO linkage used as backbone of SPE
- 2000s: Functionalized phosphazenes used as flame-retardants

Stability and Safety

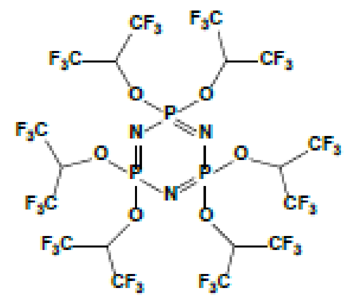


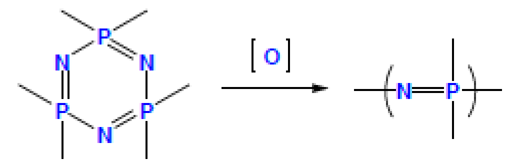




Idaho Nat'l Lab
PI: Gering

High voltage additive with F-alkyl





- tendency to polymer exploited
- actual cell tests vary
- no obvious advantage to phosphates or aluminates

Army Research Lab
PI: Jow/Xu

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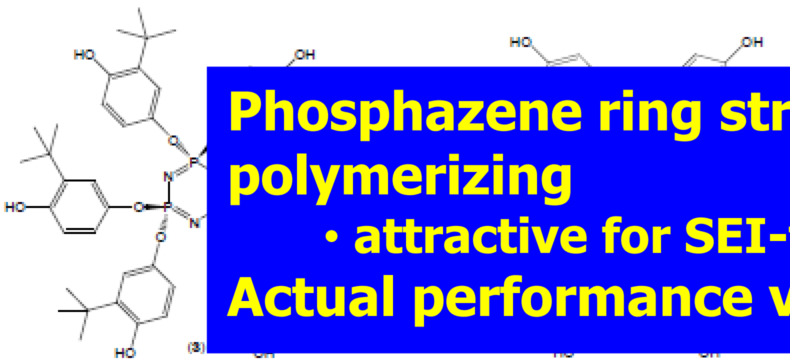
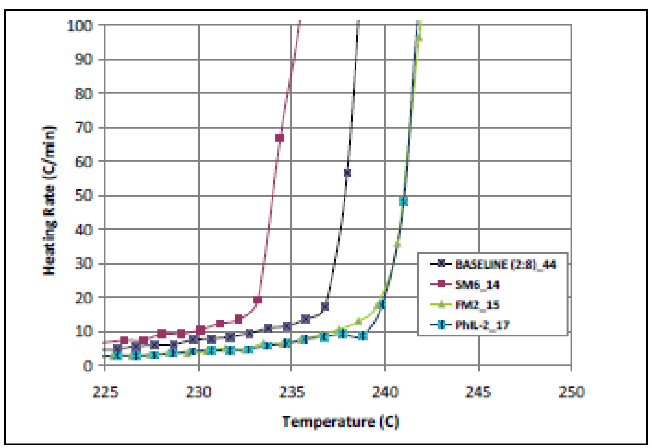


Phosphazene ring structure affords the possibility of polymerizing

- attractive for SEI-film designers

Actual performance varies



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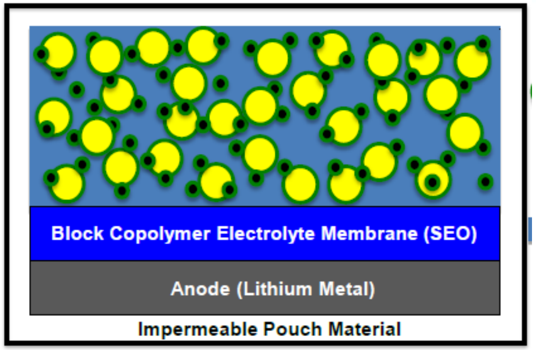
TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

Block Co-polymer Electrolyte for Li-Metal Battery

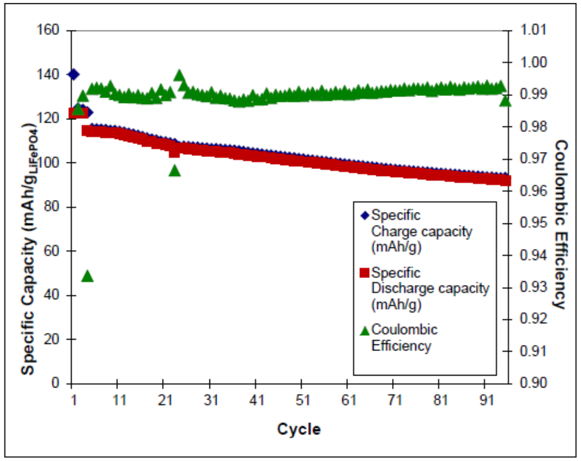


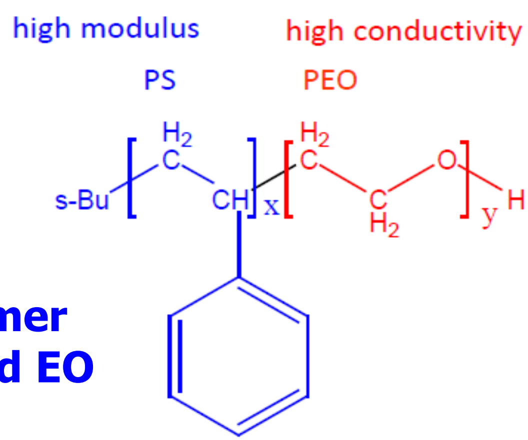
Advantage:

- mechanical and conductive functions decoupled
  - Li dendrite could be prevented
  - decent ion conductivity

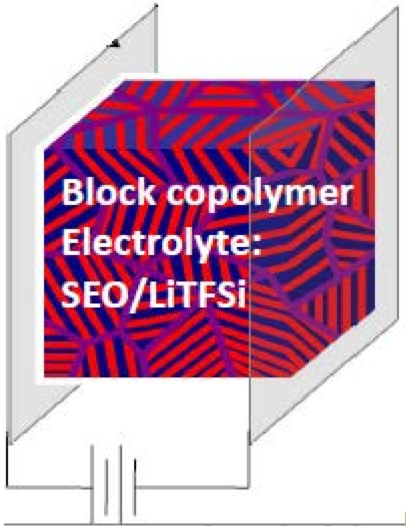
Disadvantage:

- Ion conductivity could only allow for HT (60~70 ºC) operation
- Anodic stability limit applied by EO-linkages





Block-copolymer of Styrene and EO



LB Nat'l Lab
PI: Balsara

Block Co-polymer Electrolyte for Li-Metal Battery

Advantage:

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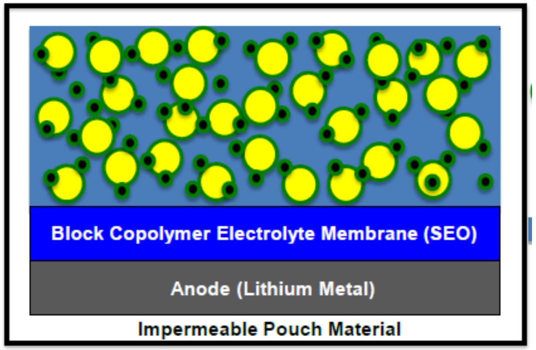
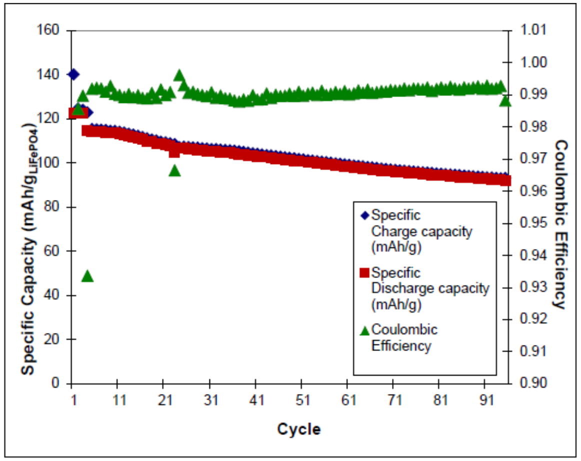
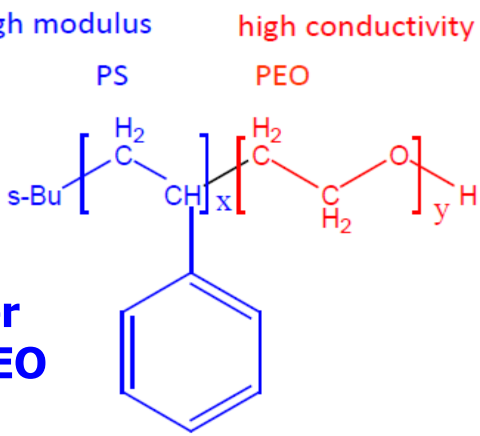
A clever niche found for LFP vs. Li Chemistry

- < 4.0 V stable region for EO links
- energy density compensation from metal Li



operation





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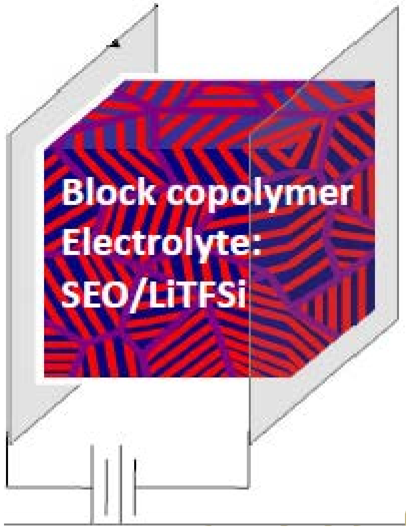


LB Nat'l Lab
PI: Balsara

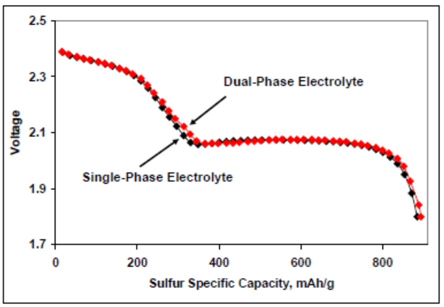
US ARMY RDECOM

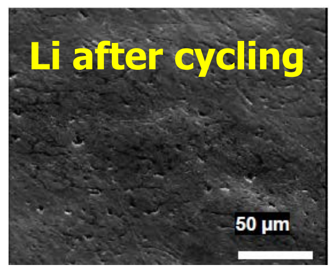
Electrolytes for Li/S and Li Aqueous Chemistries

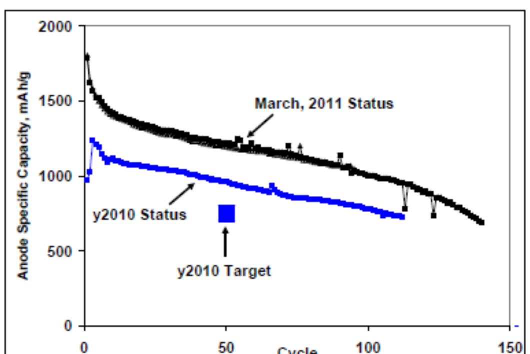
ARL

Dual-phase Electrolyte: Li protection

- anolyte: Li_2S_8 insoluble; immobilized in polymer gel
- catholyte: solubilize polysulfides

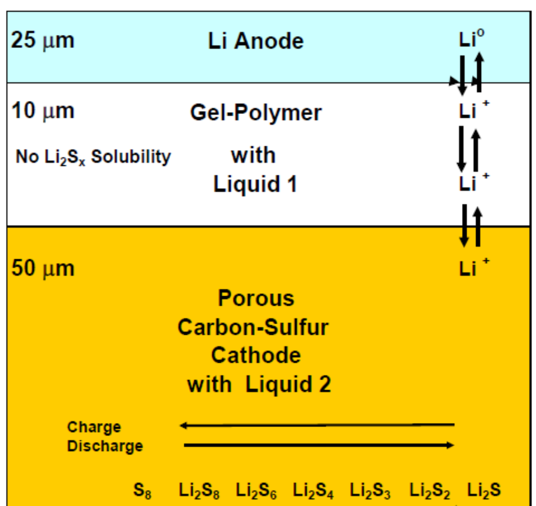






Anode specific capacity vs cycle.

Dual Phase Electrolyte Li-S Battery

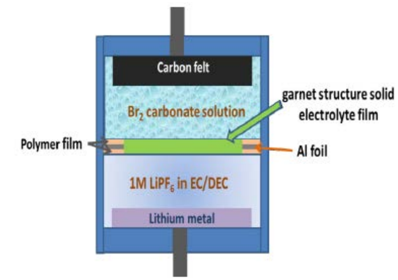


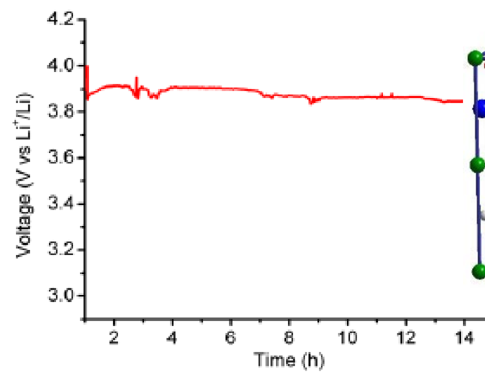
Sion Power

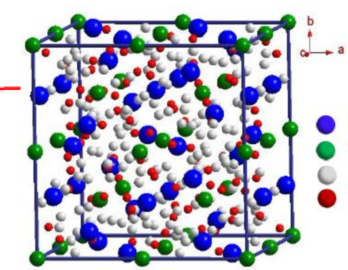
Sion Power
PI: Mikhaylik

Solid Electrolyte: Garnet structure

- stable vs. Li
- $\sigma > 10^{-3}$ S/cm
- thin/strong film
- Li/Br_2 cell







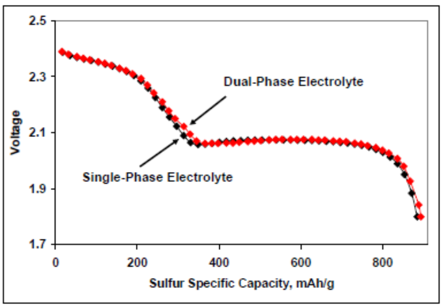
UT-Austin
PI: Goodenough

Electrolytes for Li/S and Li Aqueous Chemistries

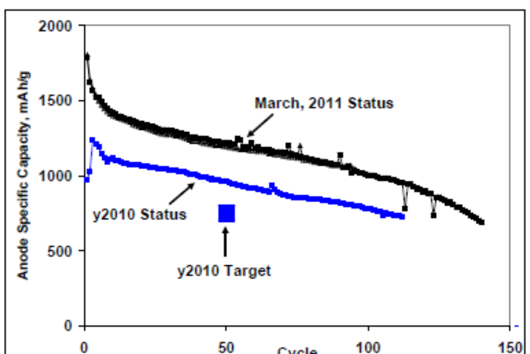
US ARMY RDECOM ARL

Dual-phase Electrolyte: Li protection

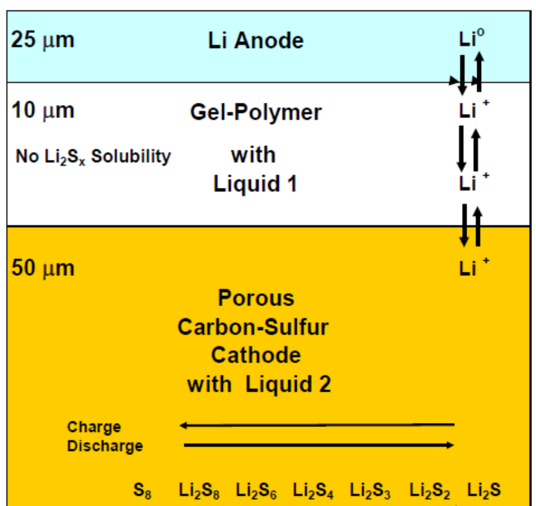
- anolyte: Li_2S_8 insoluble; immobilized in polymer gel
- catholyte: solubilize polysulfides



Li metal protection still the key in realizing Li/S chemistry



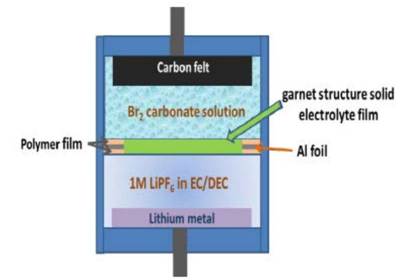
Anode specific capacity vs cycle.

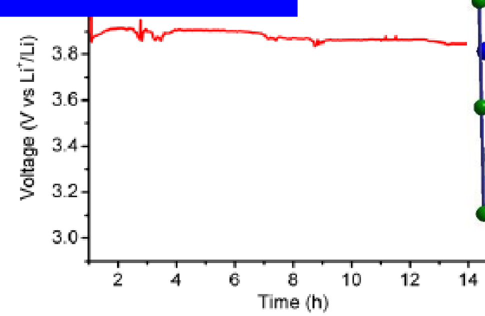


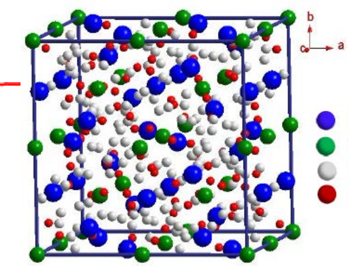
Sion Power
PI: Mikhaylik

Solid Electrolyte: Garnet structure

- stable vs. Li
- $\sigma > 10^{-3}$ S/cm
- thin/strong film
- Li/Br_2 cell







UT-Austin
PI: Goodenough

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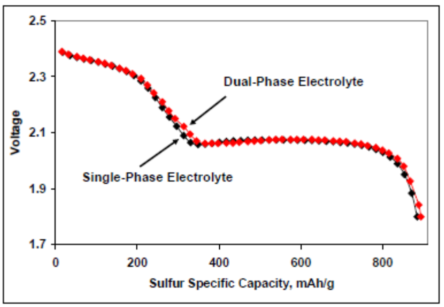

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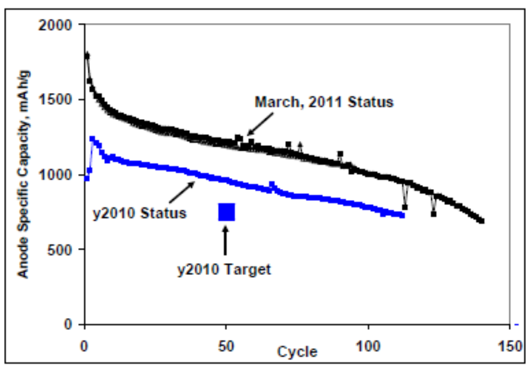

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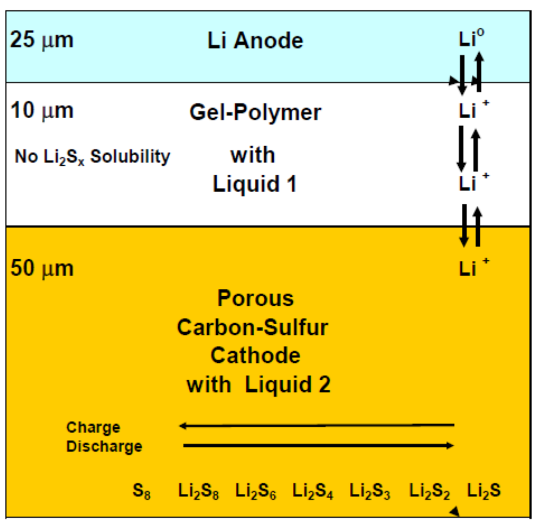

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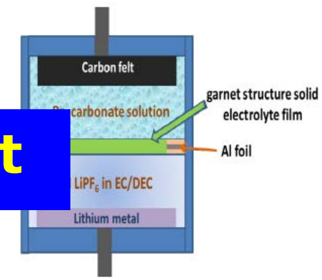
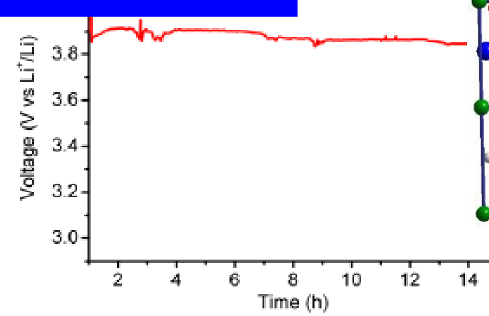
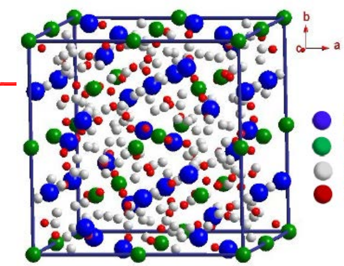


Scale-up and cost





UT-Austin
PI: Goodenough

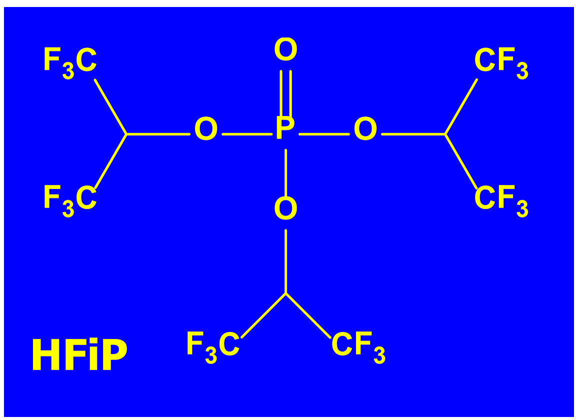
US ARMY RDECOM

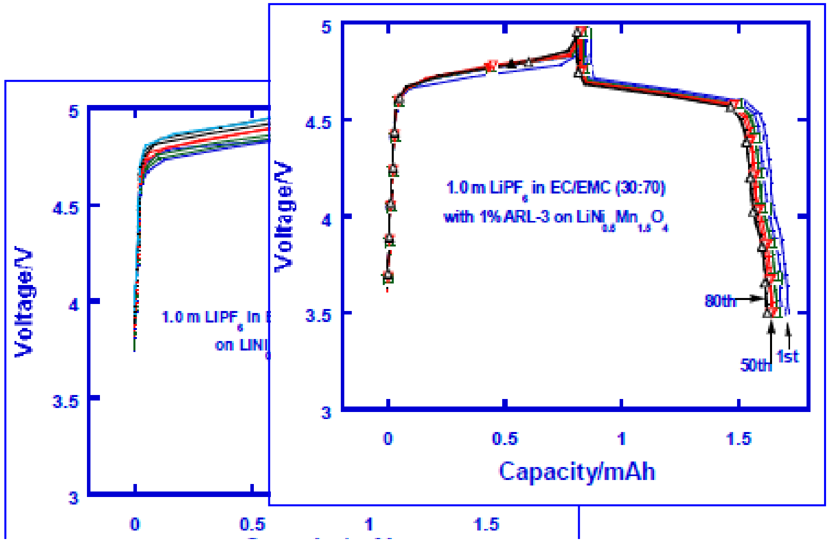
High Voltage Electrolyte: Additive Approach

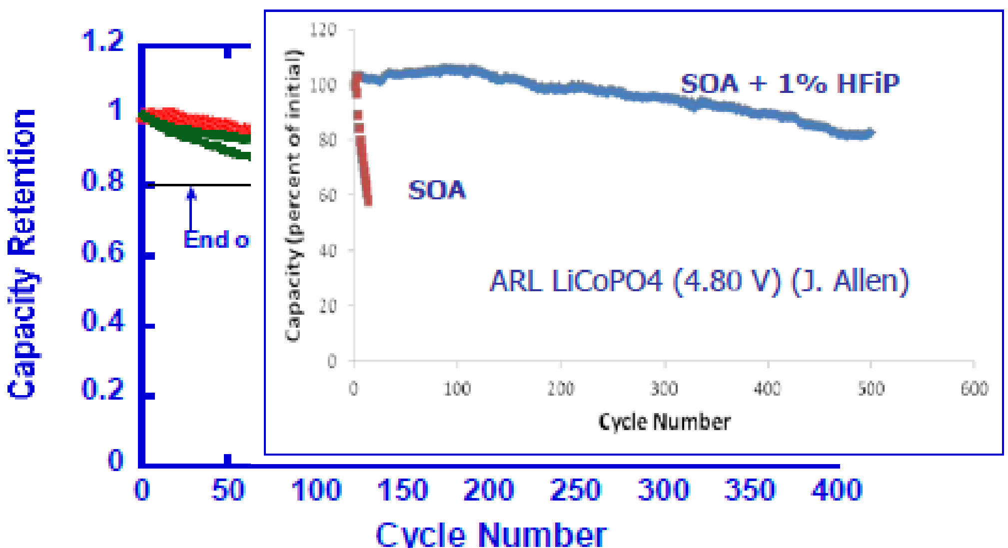
ARL

Additive Approaches

- **maintaining bulk electrolyte composition**
- **sacrificial additives dictates interphasial chemistry**
    - **fluoroalkyl phosphates identified as first family of such additives**



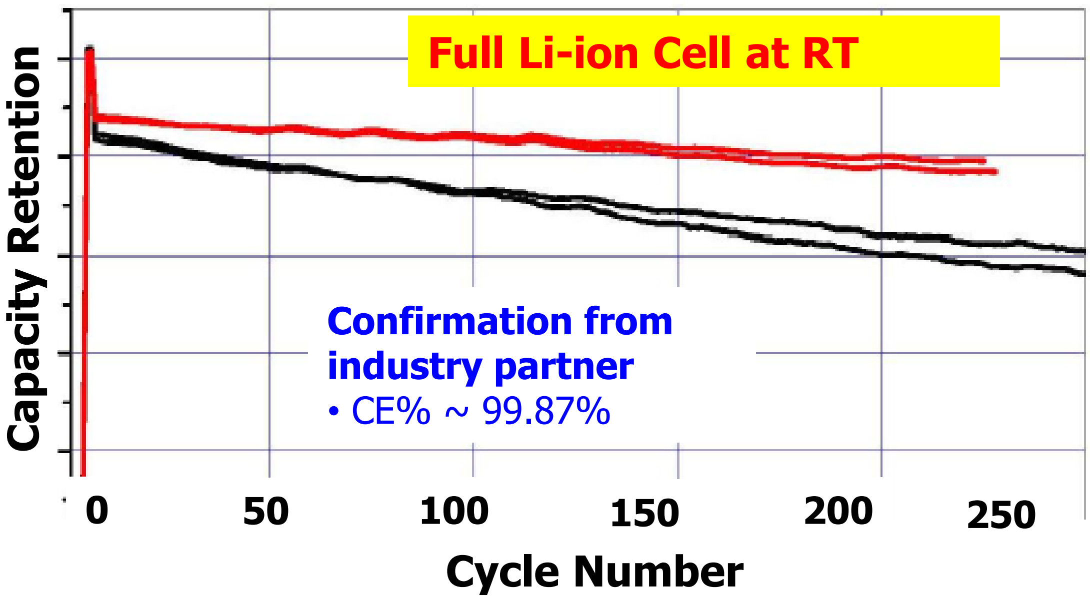




ARL **Army Research Lab**
PI: Jow/Xu

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

Full Cells Confirmation Scale-up/Characterization/Design of New Additives



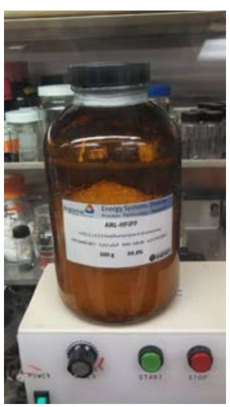
LMNO spinel (ARL2) vs. Graphite (ARL2)
formation, 1C, 3.5 to 4.95V,
BatCell, HVP/B2Cu, GF, RT
1.2M LiPF6 in EC/EMC 3:7

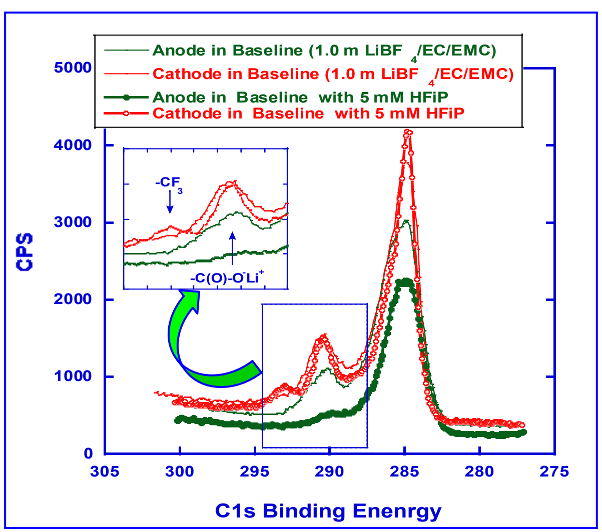
blank
0.3 wt% HFiP (sublimated, ex ARL)

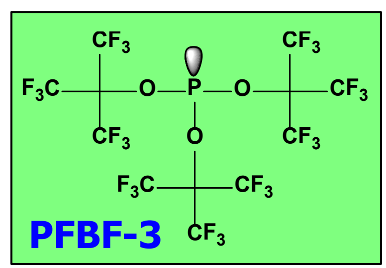
Results confirmed in full Li ion cells
- **LMNO cathode and Graphite anod**

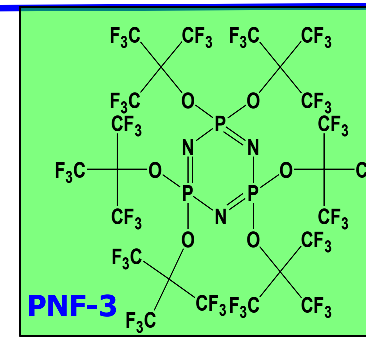
Large cell configuration
Longevity cycling at RT
CE% approaching the goal of 99.99%

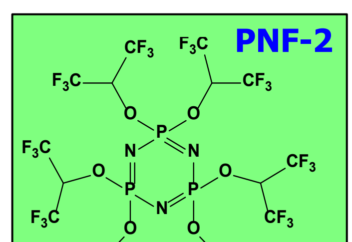
HFiP scaled-up at ANL facility
POC: Dr. Krumdick

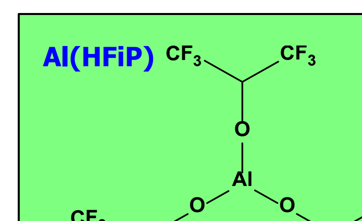










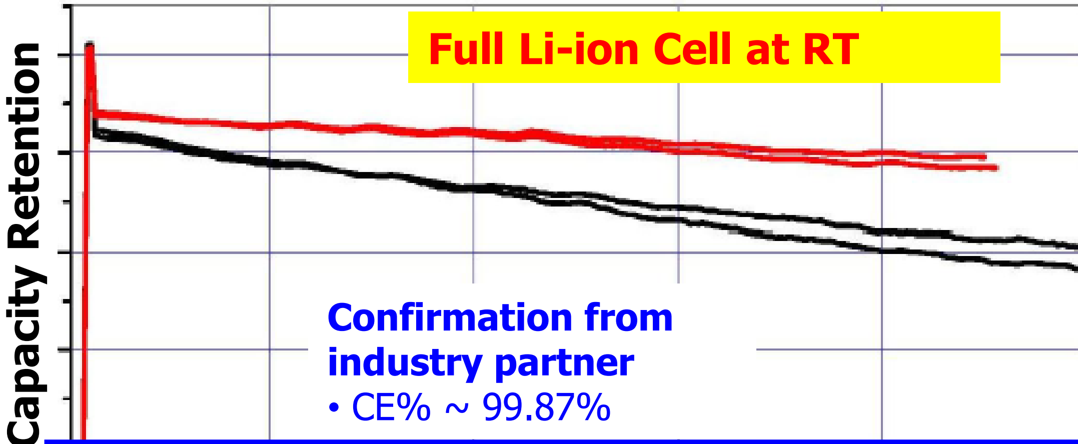


Army Research Lab

Full Cells Confirmation Scale-up/Characterization/Design of New Additives

US ARMY RDECOM

ARL



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BatCell, HVP/B2Cu, GF, RT
1.2M LiPF6 in EC/EMC 3:7

blank
0.3 wt% HFiP (sublimated, ex ARL)

Confirmation from industry partner

- CE% ~ 99.87%

Results confirmed in full Li ion cells

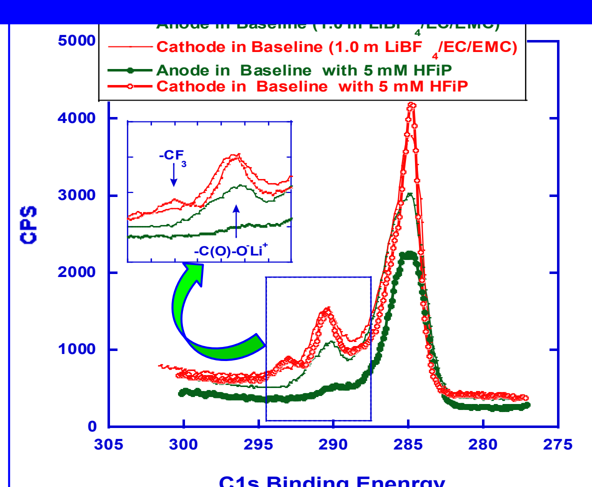
- LMNO cathode and Graphite anod
- ell configuration
- ity cycling at RT
- pproaching the goal of 99.99%

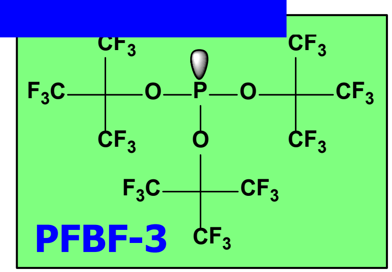
Capacity fading at HT still an issue

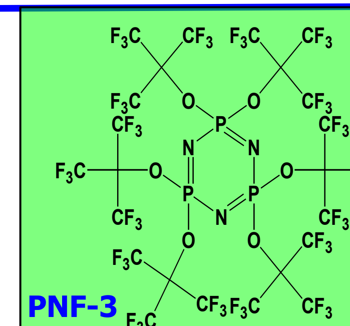
- **involving both electrode and electrolyte**

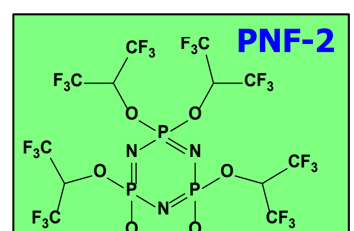
Better additive to be developed.

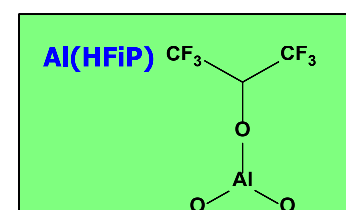
HFiP scaled-up at ANL facility
POC: Dr. Krumdick









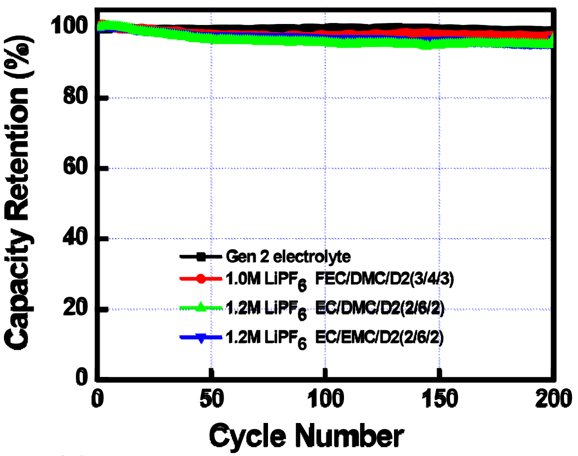


ARL
Army Research Lab

High Voltage Electrolyte: Solvent Approach

- Improved stability at 55°C demonstrated using $LiNi_{0.5}Mn_{1.5}O_4$/LTO chemistry
- Interfacial issue with graphite anode at high temperature
- Electrolyte formulation and/or new SEI formation: further improve the high V. performance
- Intrinsic stability combined with kinetic stability on both electrode/electrolyte interfaces

RT

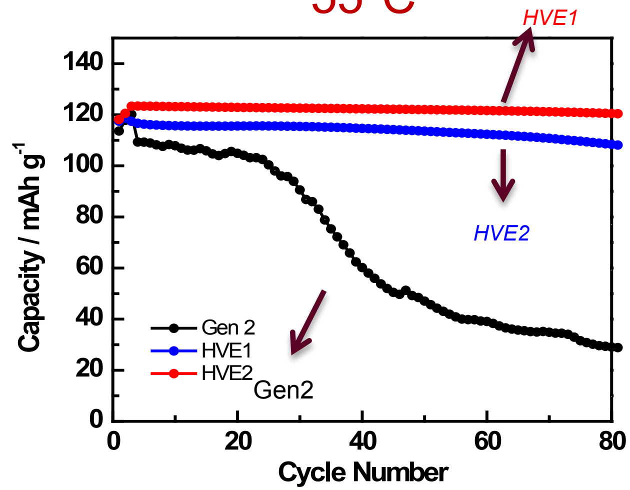


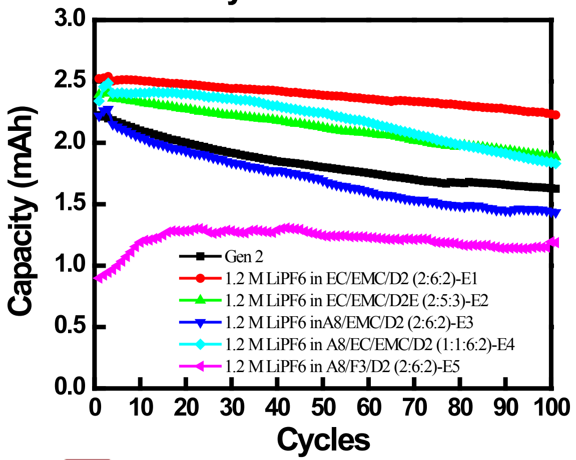
LTO/LNMO Couple

(3.45-2.0V)

Gen 2 electrolyte (1.2 M LiPF6 EC/EMC (3/7)
1.0M LiPF6 FCC/FLC/FE (3/4/3) – HVE1 (E5)
1.2M LiPF6 FCC/EC/FLC/FE (2/6/2) – HVE2
1.2M LiPF6 EC/DMC/FE(2/6/2) – FE-1
1.2M LiPF6 EC/EMC/FE(2/6/2) – FE-2

55°C





Graphite/LNMO Couple

(4.9-3.5)

Gen 2 electrolyte (1.2 M LiPF6 EC/EMC (3/7)
1.0M LiPF6 FCC/FLC/FE (3/4/3) – HVE1 (E5)
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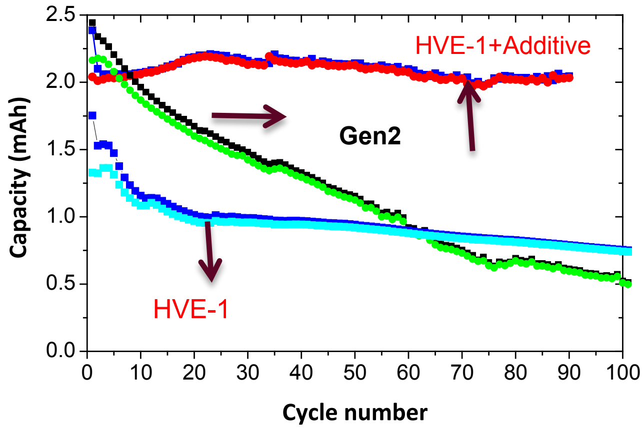
1.2M LiPF6 EC/EMC/FE(2/6/2) – FE-2



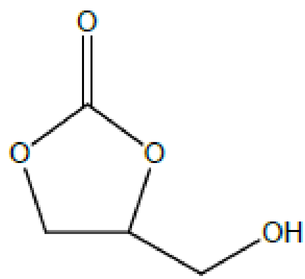
Argonne Nat'l Lab
PI: Zhang

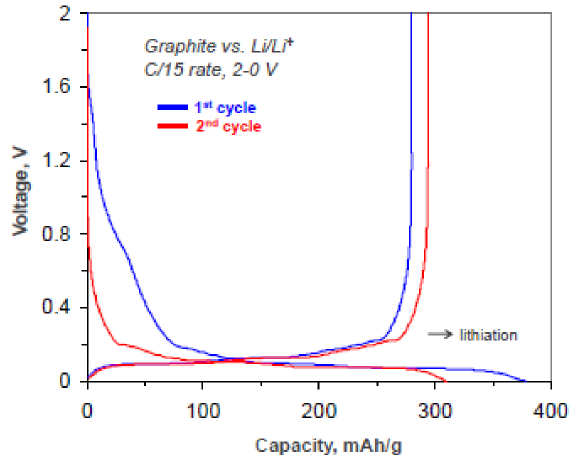
New Electrolytes: EC-Derivatives

Investigate novel electrolytes that include glycerol carbonate, and its modifications: methyl, ethyl ethers, and oligo(ethylene oxide) ethers.

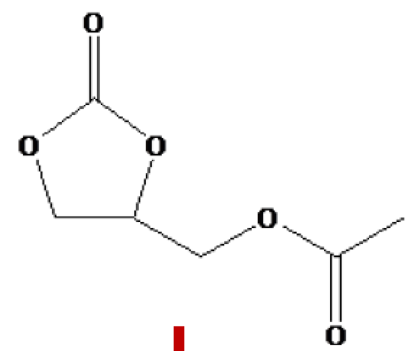
- Stability issues on both electrode
- Li salt effect on SEI formation

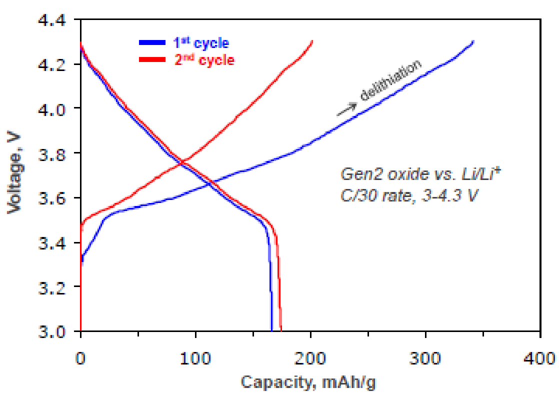
Glycerol carbonate

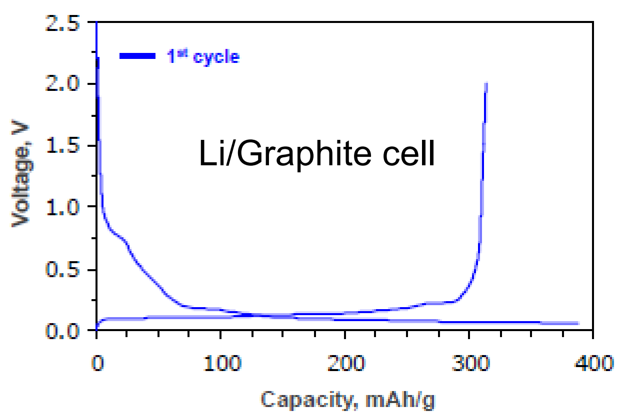


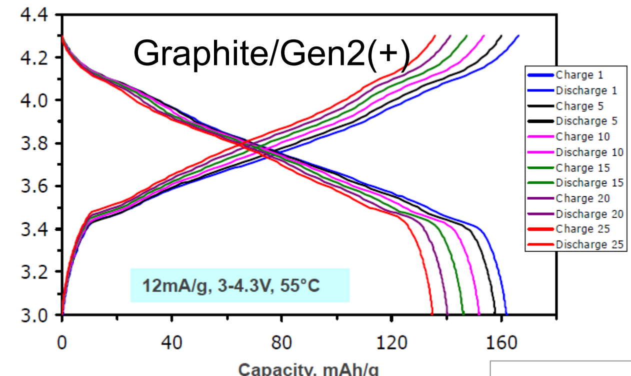


Modified glycerol carbonate









Argonne Nat'l Lab
PI: Abraham

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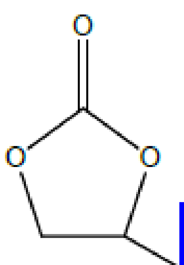

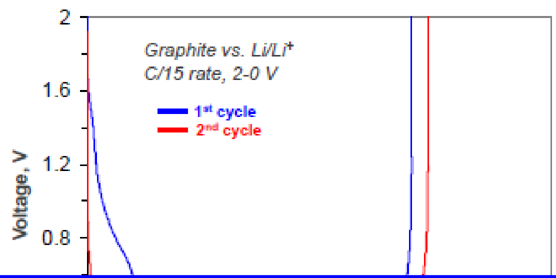

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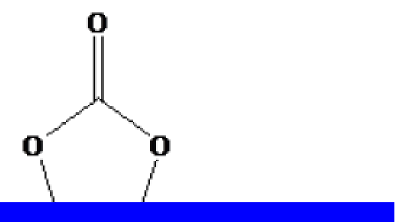
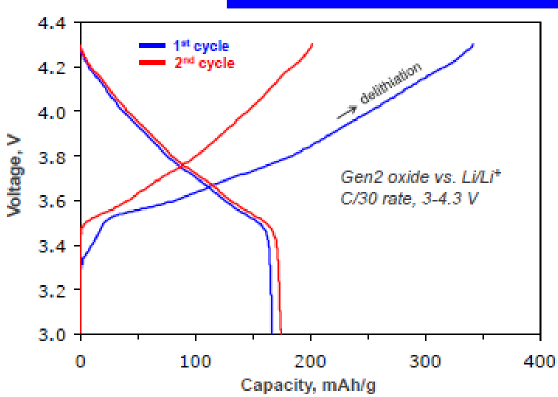
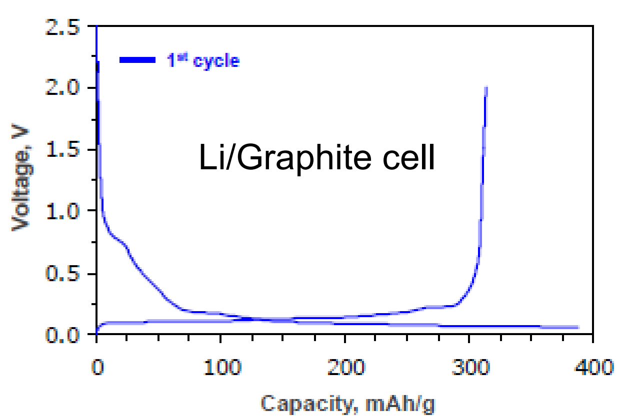
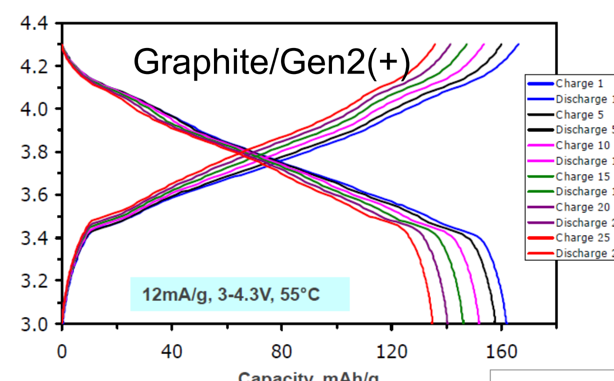


Structure modification of GC showed improved compatibility on both electrode.

Cycling performance needs to be improved at RT.
SEI additives are mandatory for both electrodes.





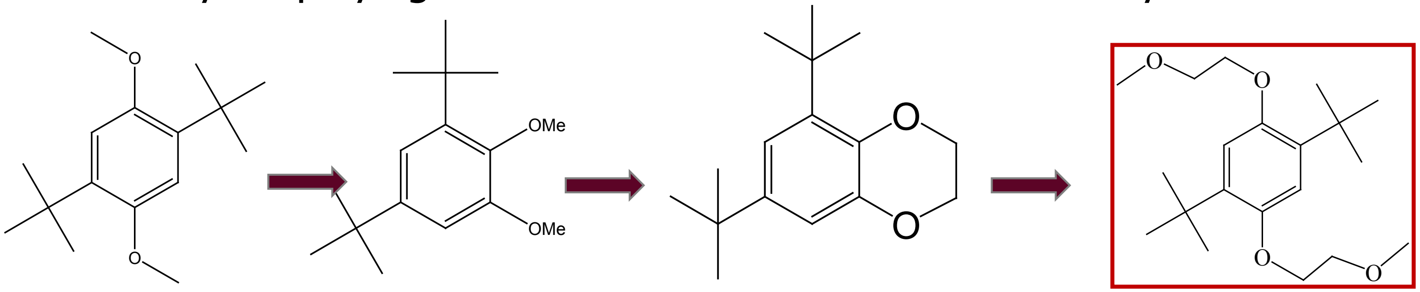


Argonne Nat'l Lab
PI: Abraham

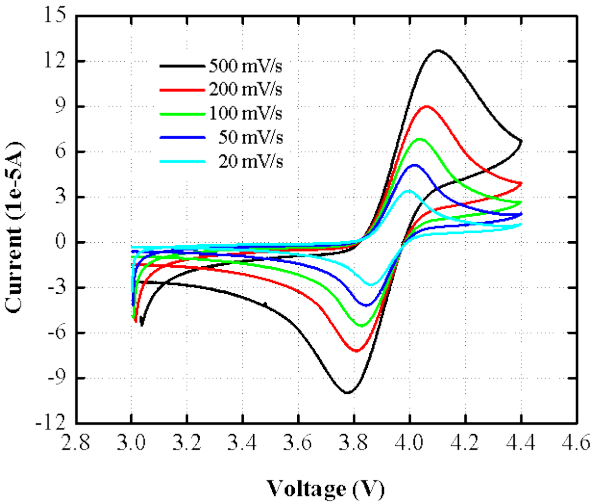
Electrolyte Additives: (1) Low Voltage Redox Shuttle

Redox shuttle additive to prevent cathode reaching dangerously high potential

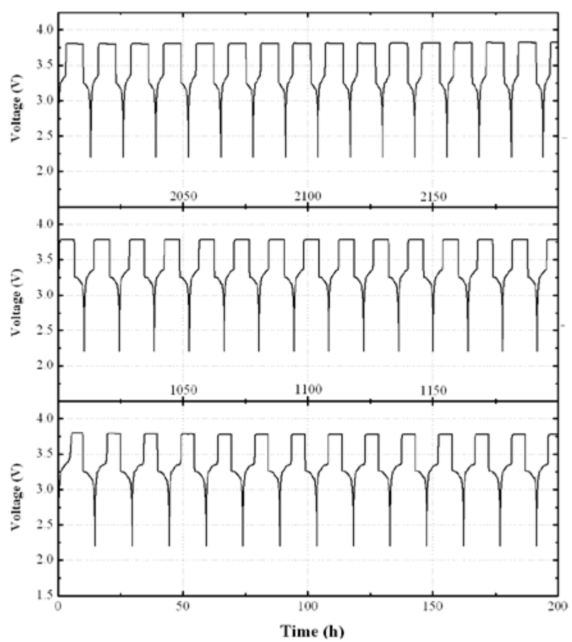
- Symmetrical structure with oligo(ethylene glycol) chain: high stability and high solubility.
- Reversible redox at 4.0V *vs* Li/Li^+: suitable for $LiFePO_4$ chemistry
- No interfere with bulk electrolyte.
- Reduce cost by simplifying the BMS: 10% reduction estimated by BatPaC v1.0.



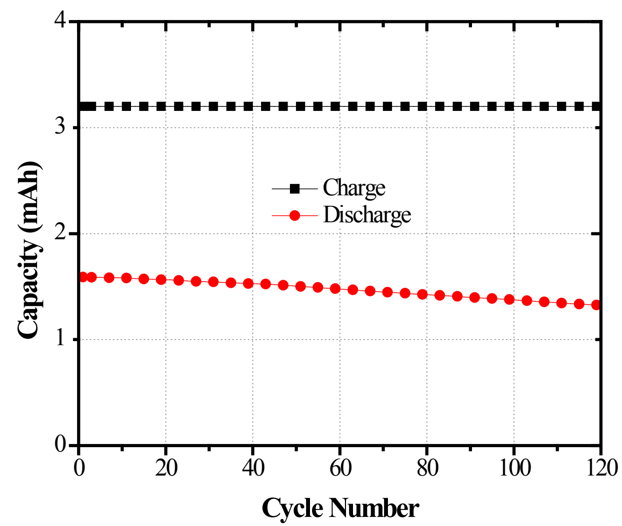
ANL-RS-2



CV profile of ANL-RS-2



Graphite/$LiFePO_4$, 100% overcharge, C/10, 0.1M RS-2 in Gen2 electrolyte



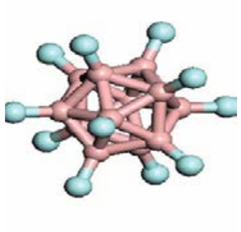
LTO/$LiFePO_4$, 100% overcharge, C/2 0.4M RS-2 in Gen2 electrolyte

Argonne Nat'l Lab
PI: Amine/Zhang

Electrolyte Additives: (2) Medium Voltage Redox Shuttle

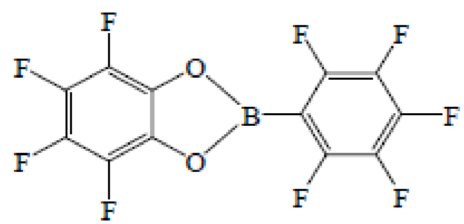
Molecular Engineering to raise the redox potential for 4V $LiMO_2$ (M=Mn, Ni, Co) cathodes

- Tunable redox potential by structure modification.
- Variety of active redox centers: benzene or borate cluster
- Electron-withdrawing substitution: lower the HOMO energy, thus increase the potential



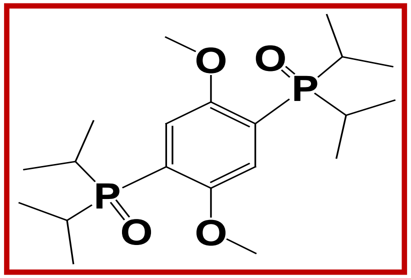
$B_{12}F_{12-x}H_x^{2-}$

4.2-4.7V

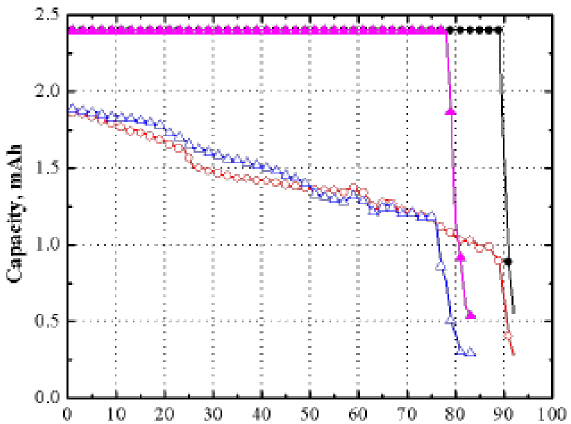


4.3V

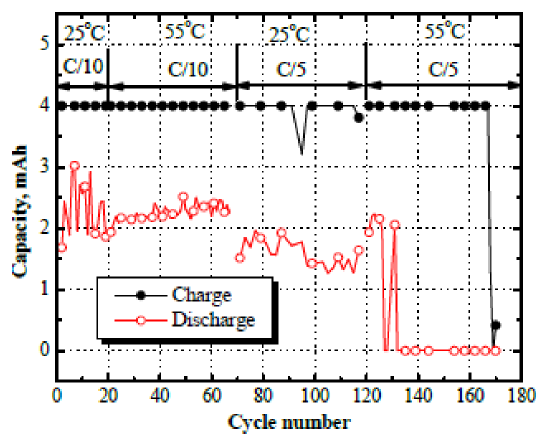
ANL-RS-5



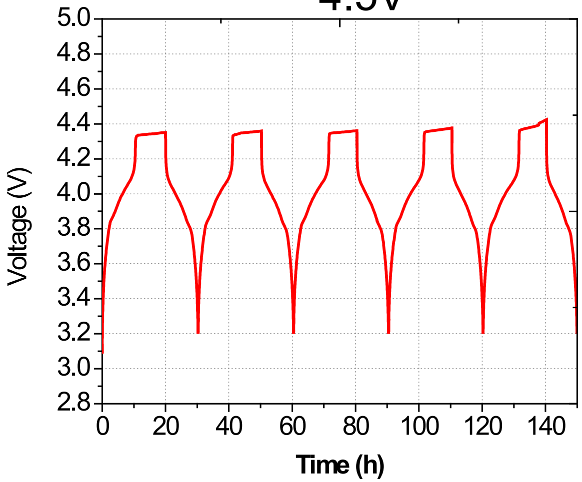
4.5V



MCMB/$Li_{1.1}(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$



MCMB/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$



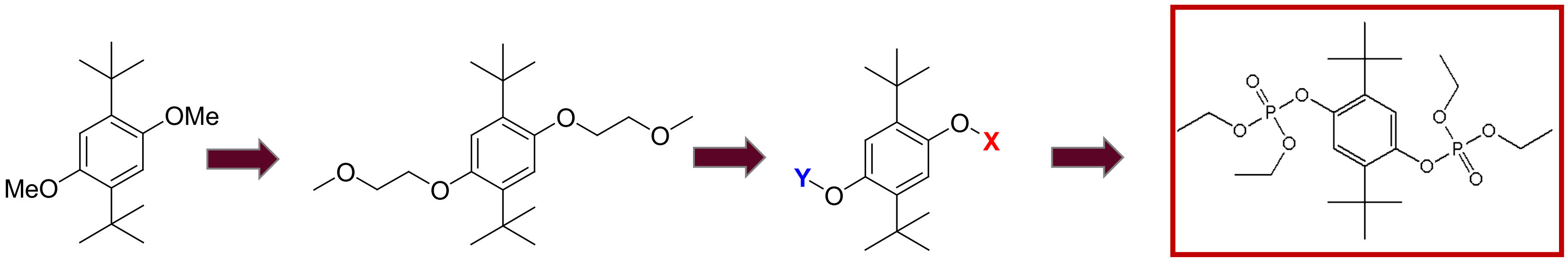
MCMB/$LiMn_2O_4$

Argonne Nat'l Lab
PI: Amine/Zhang

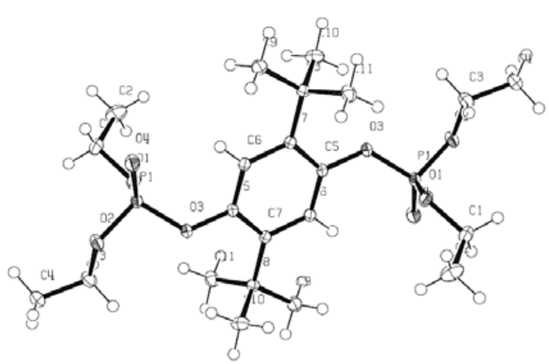
Electrolyte Additives: (3) High Voltage Redox Shuttle

Molecular Engineering to further raise the redox potential for high voltage cathodes (LNMO)

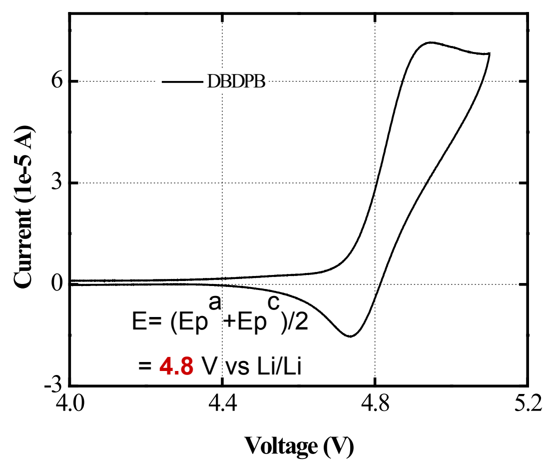
- Introduce strong electron-withdrawing group to further lower the HOMO energy
- Overcharged protection at 4.8V vs Li/Li^+ demontrated.
- Performance degradation due to the possible electrolyte instability at high redox potential
- Need high voltage electrolyte to full identification



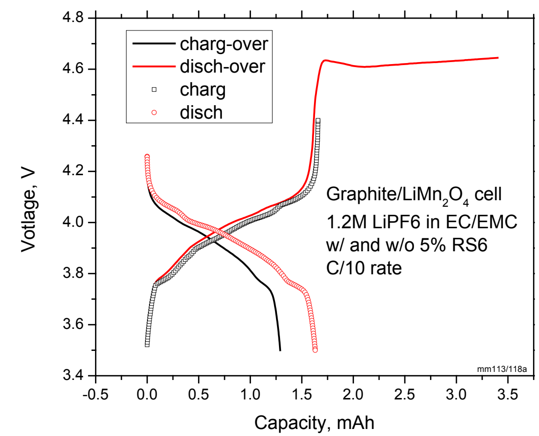
ANL-RS-6



Single crystal structure



CV profile in Gen2 electrolyte



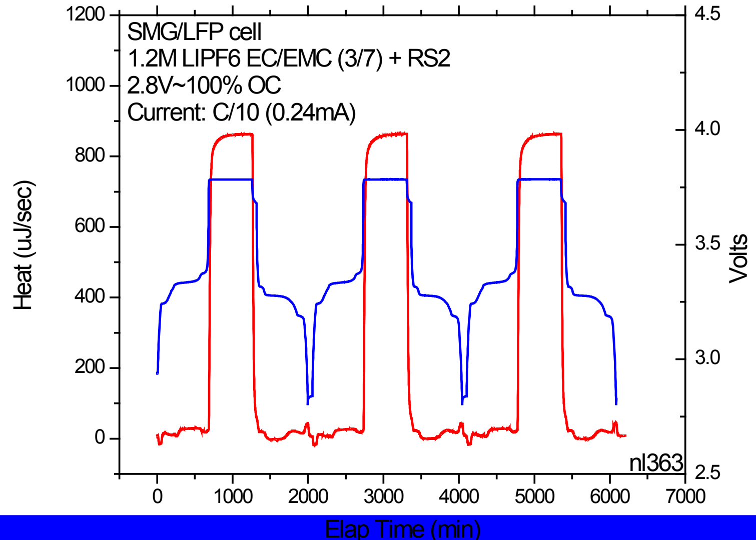
Overcharge test
$LiMn_2O_4$/Gen2 electrolyte

Argonne Nat'l Lab
PI: Amine/Zhang

Electrolyte Additives: (3) High Voltage Redox Shuttle

Molecular Engineering to further raise the redox potential for high voltage cathodes (LNMO)

- Introduce strong electron-withdrawing group to further lower the HOMO energy
- Overcharged protection at 4.8V vs Li/Li^+ demontrated.
- Performance degradation due to the possible electrolyte instability at high redox potential
- Need high voltage electrolyte to full identification



Many advantages to apply redox shuttle in PHEV batteries (overcharge abuse tolerance, low cost, cell self-balancing…)

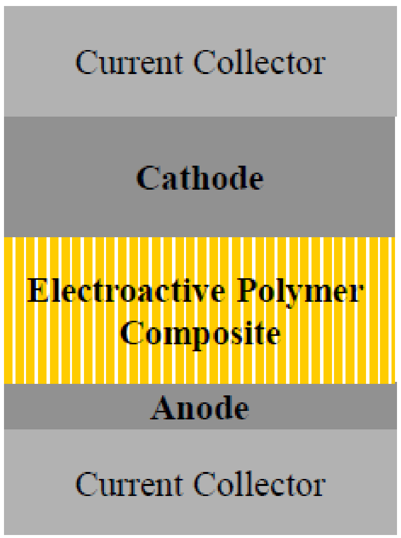
Heat generation during overcharging process.
Need to be coupled with Thermal Management System to dissipate heat, especially under high current overcharging abuse!

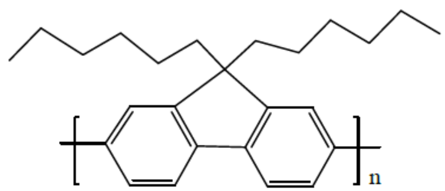
Argonne Nat'l Lab
PI: Amine/Zhang

Electroactive Polymer for Overcharge Protection

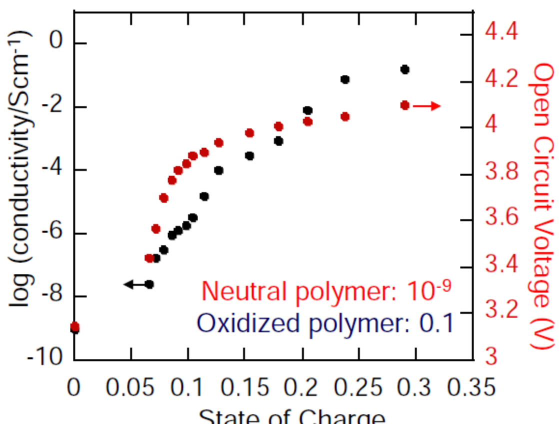
Incorporating electroactive polymer for overcharge protection

- Reversible redox reaction accompanied by drastic change in electronic conductivity
- Resistive internal short providing a current bypass; the cell potential within a safe range
- Good rate capability (5C) achieved for fiber-based composite separator
- Versatile as cell holding potential is varied by the choice of polymer, polymer morphology and distribution, system configuration; Capable of low temperature protection

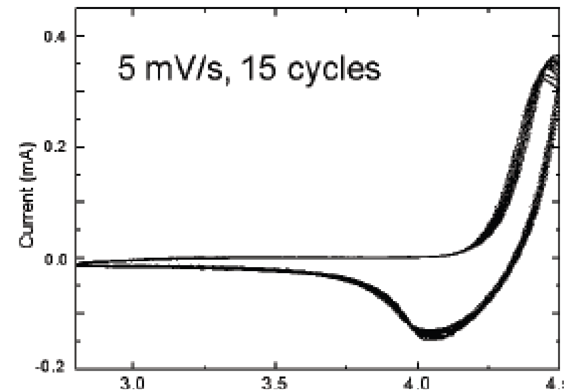


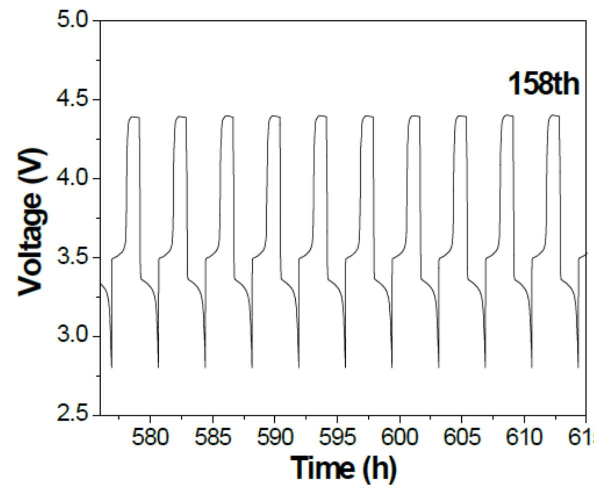


Poly(9,9-dioctylfluorene) (PFO)



SOC dependent conductivity



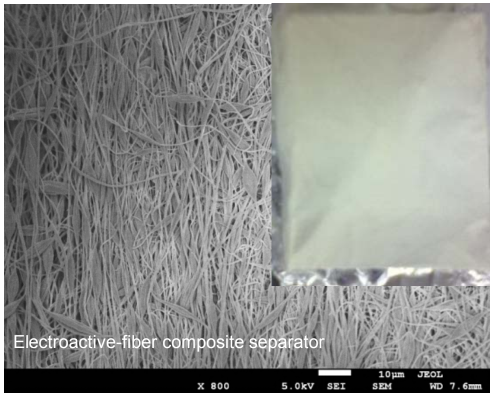


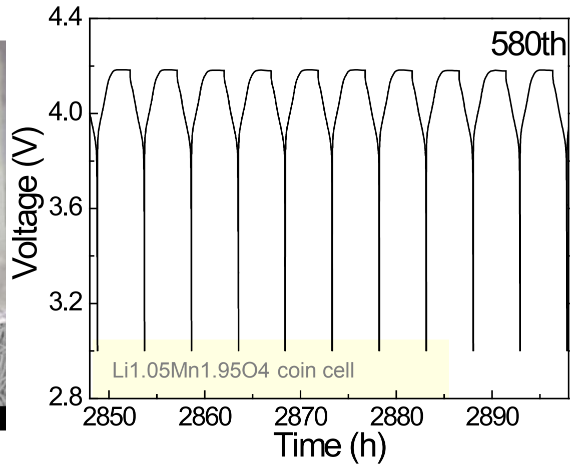
20% overcharge, Li/$LiFeO_4$

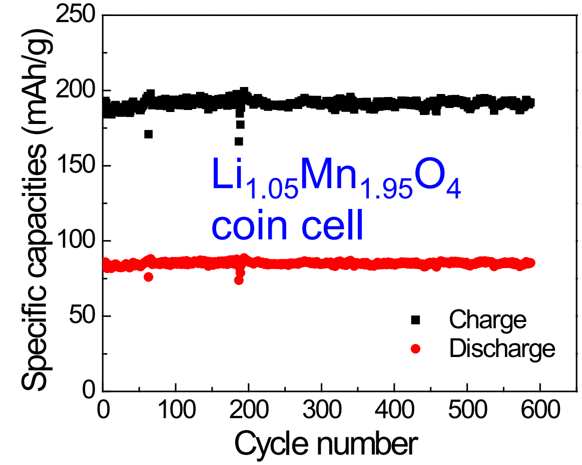
LBL, PI: Richardson/Chen

Electroactive Polymer for Overcharge Protection

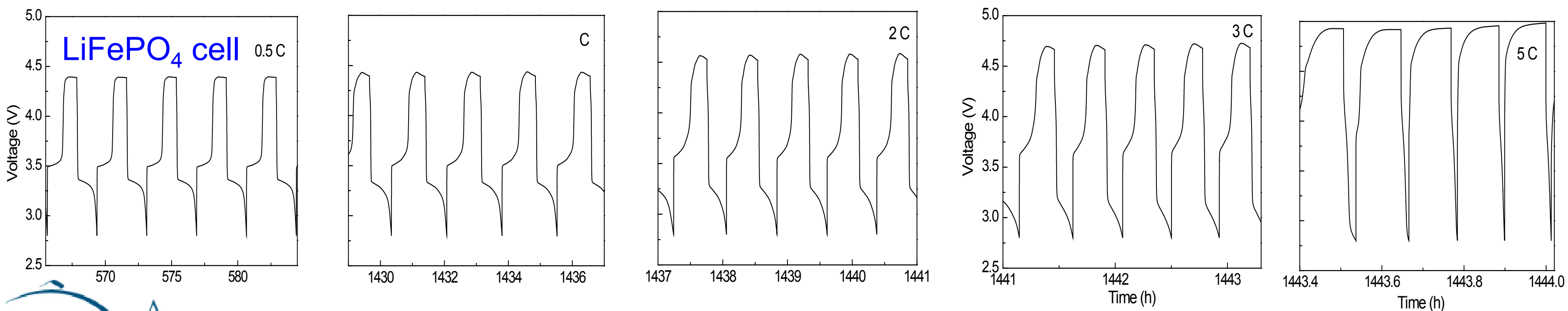
- Improvement on protection stability was achieved on highly uniform electroactive-fiber composite separators prepared by electrospinning. Most stable reversible overcharge protection in several cell chemistries was demonstrated.







- Scale-up feasibility was demonstrated on larger-sized pouch cells.



LBL PI: Richardson/Chen

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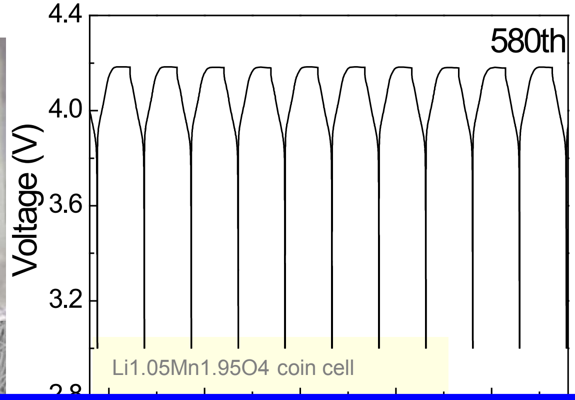
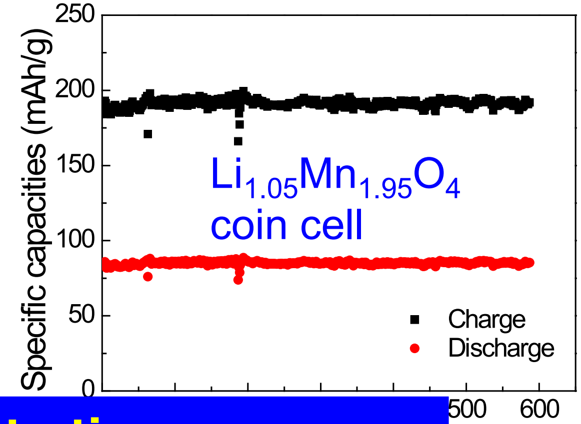
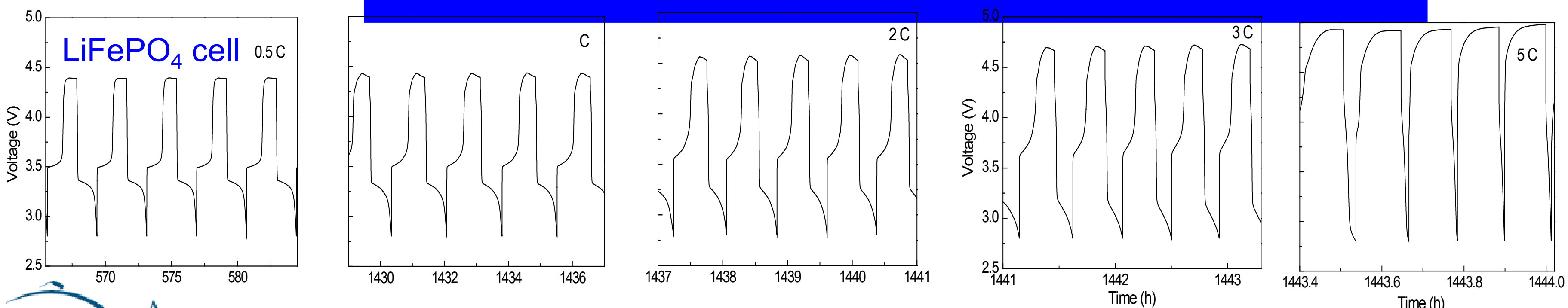




Capable of high rate overcharge protection

Complexity for incorporation into the cell (separator)
Heat generation also a potential issue

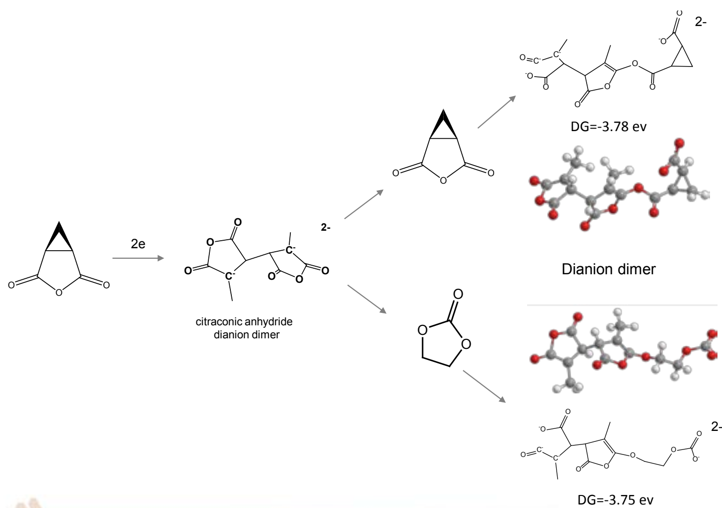
- Scale-up feasibility w



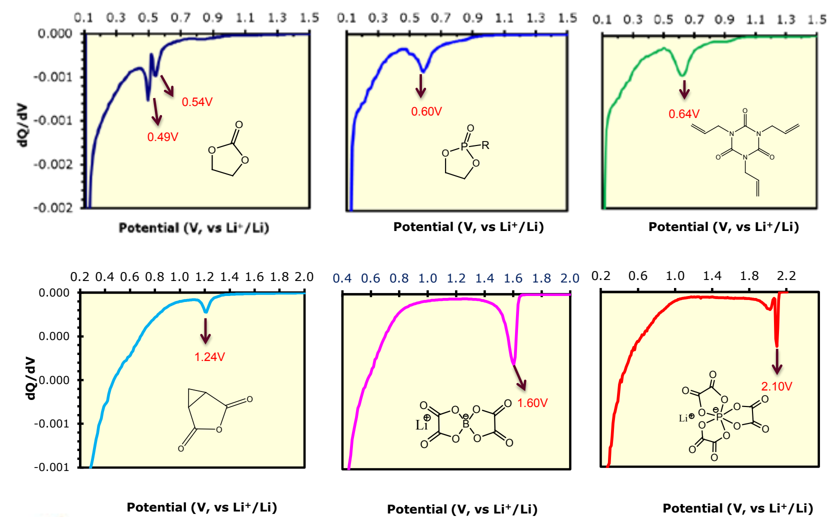
Electrolyte Additive: SEI Formation Additive

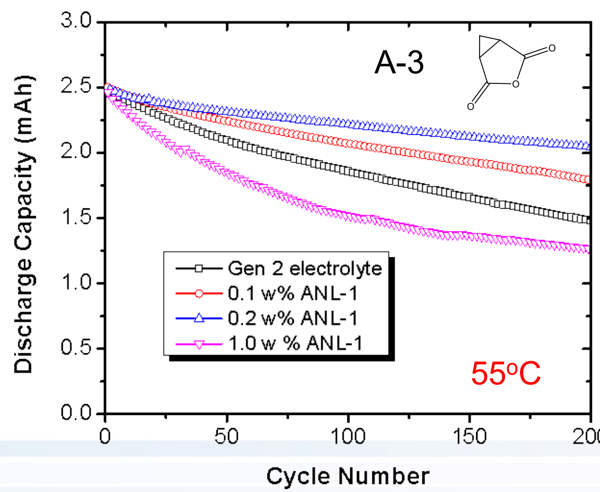
SEI formation additives to stabilize the anode/electrolyte interphase

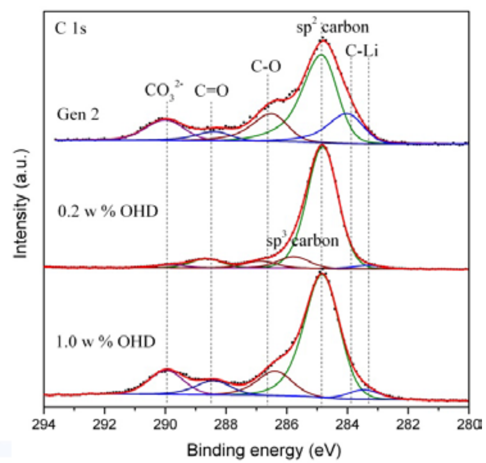
- Quantum chemical calculation (DFT and MD): reduction potential, SEI formation pathway
- Empirical rule to narrow down the selection: unsaturated bonds and functional groups
- Reductively decomposed in a preferential pathway
- Electrochemical performance validation



SEI Formations at Different Potentials (vs Li^+/Li)





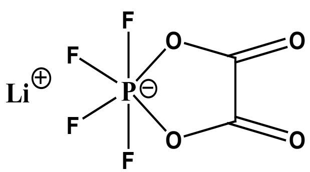


Argonne Nat'l Lab
PI: Zhang

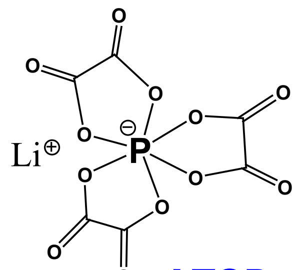
Electrolyte Additive: SEI Formation Additive

Inorganic SEI formation additive: LTFOP and LTOP

- Extended cycle life at elevated temperature
- Improved calendar life; minimal impedance increase before and after cycling
- Thermally stable SEI formation, enhanced cell safety

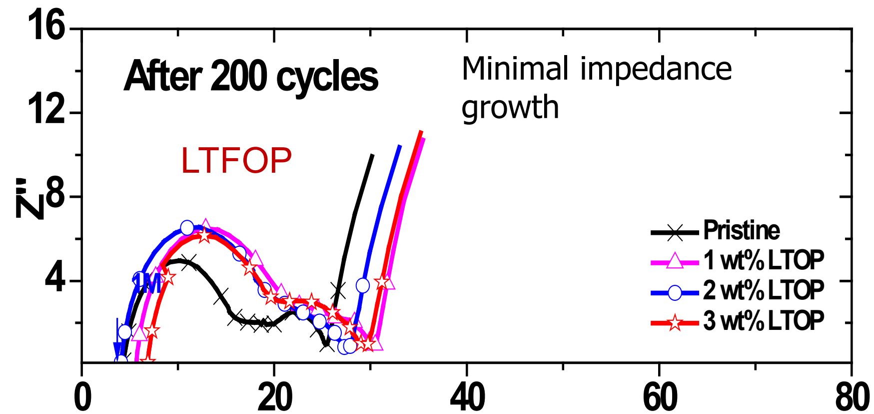


LTFOP

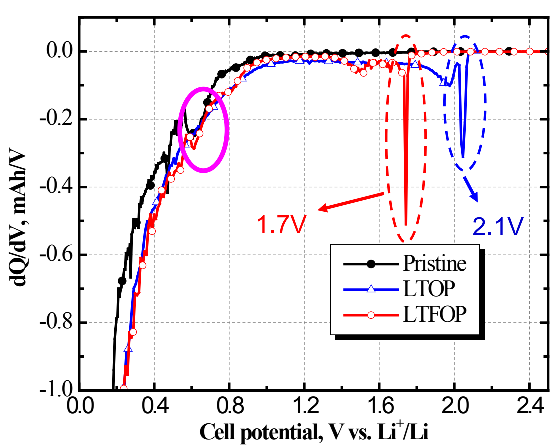


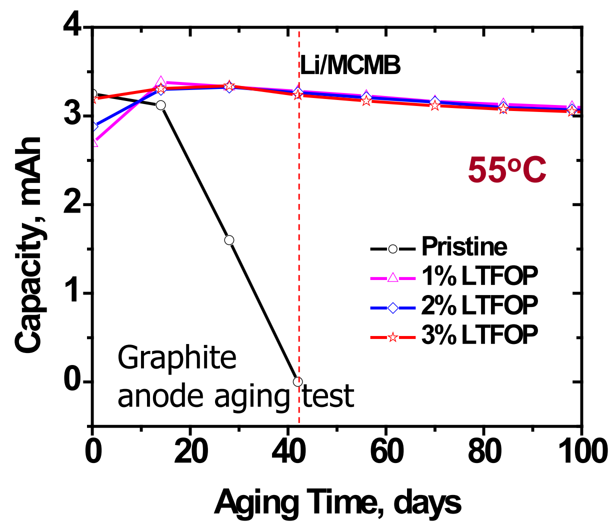
LTOP

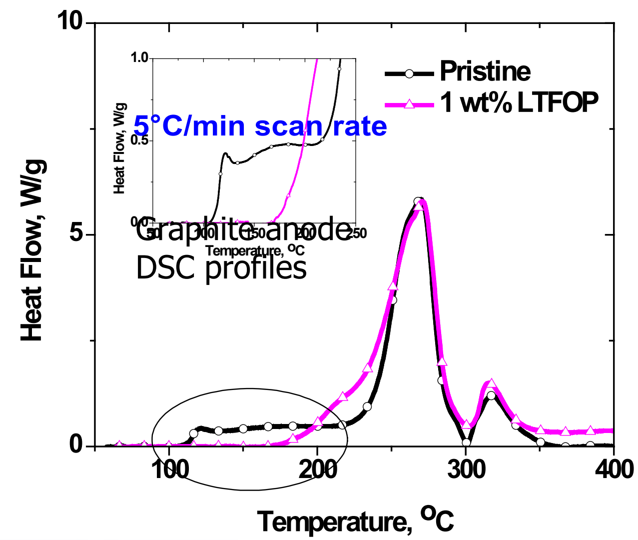
Lithium tetrafluoro(oxalato) phosphate (LTFOP)
Lithium tris(oxalato) phosphate (LTOP)



dQdV profiles of LTFOP and LTOP







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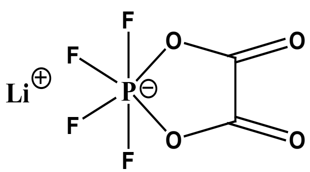
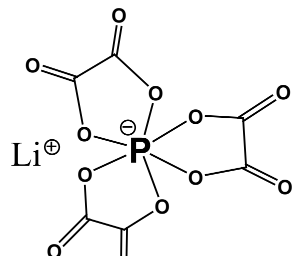
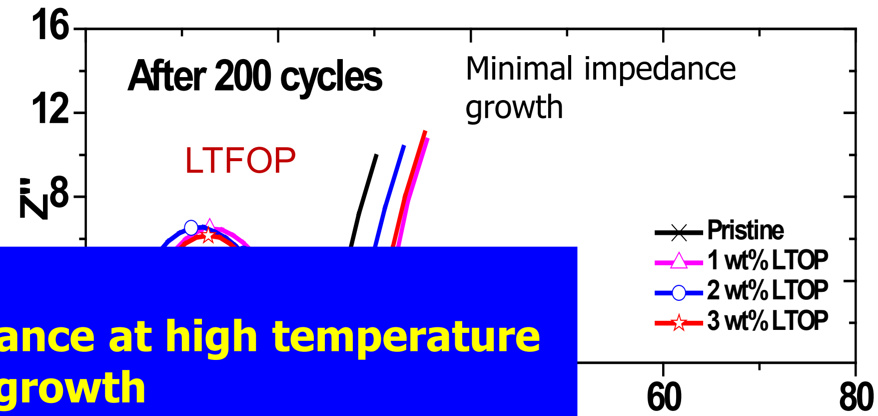


LTFOP



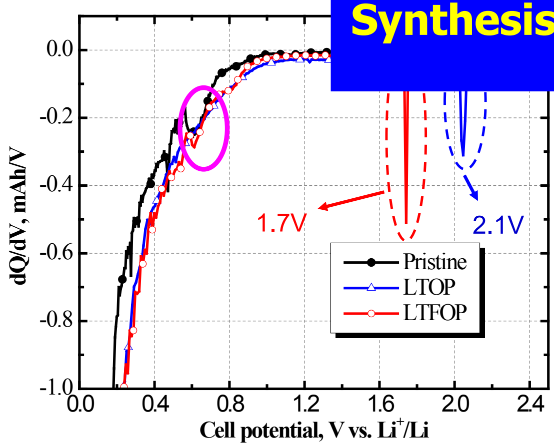


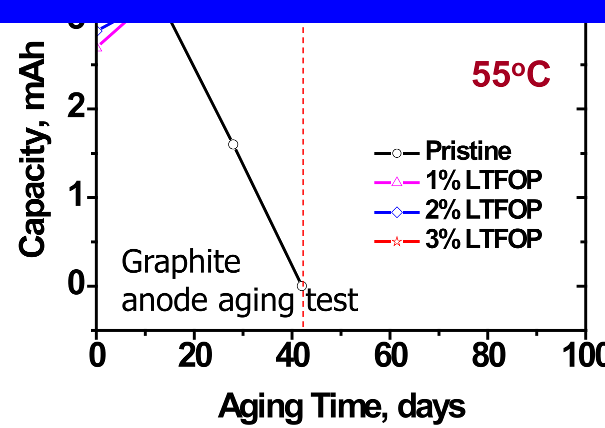
Lithium tetrafluo
Lithium tris(oxal

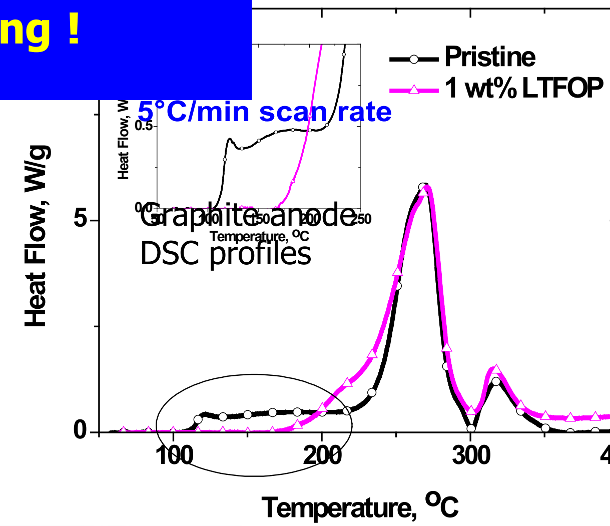
Improved cycling performance at high temperature
No significant impedance growth

Low temperature and power capability?
Synthesis/purification might be challenging !

dQdV profiles of LT







Argonne Nat'l Lab
PI: Zhang

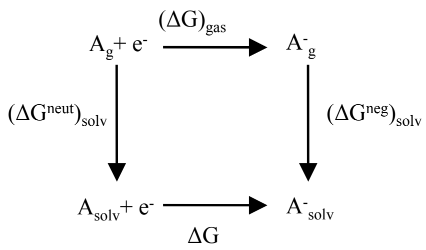
Highly Accurate Quantum Chemical Modeling: Discovery and Understanding of Electrolyte/Additive

Reduction/oxidation/potentials: Accurate calculation of electron affinity (ionization potential) + inclusion of solvation effects using a continuum model/explicit solvent molecules

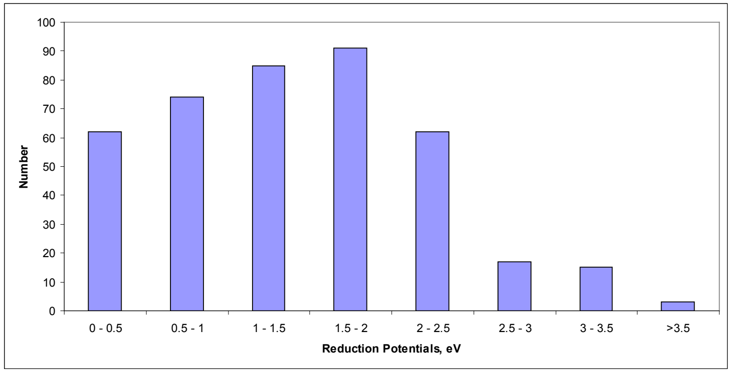
Energetics of reaction pathways for decomposition of additives for electrolytes

SEI growth from decomposition of the additives: Periodic DFT studies; polymerization of decomposition fragments

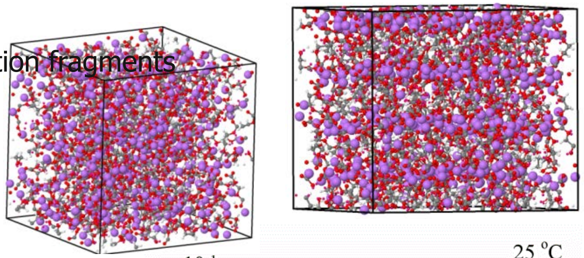
Thermodynamic Cycle Used to Calculate Reduction Potentials

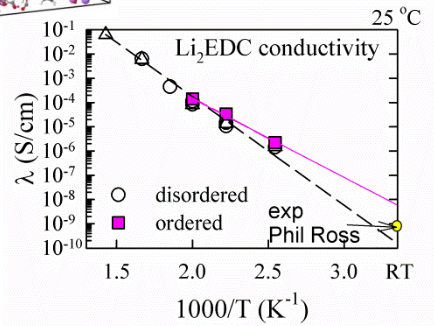


$$\Delta G = (\Delta G)_{gas} + (\Delta G^{neg})_{solv} - (\Delta G^{neut})_{solv}$$

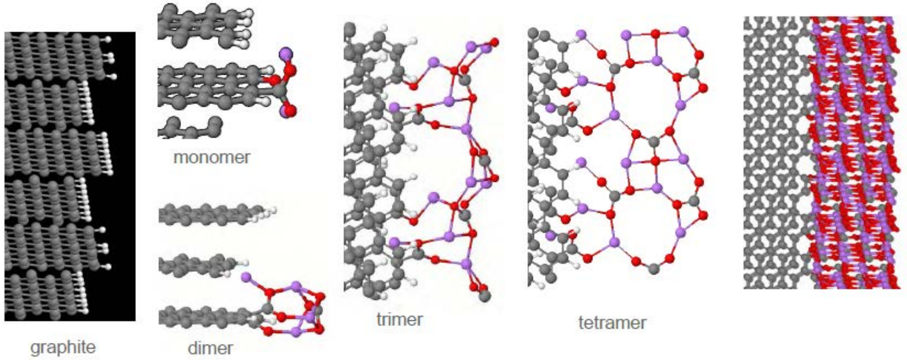


Bar chart showing the distribution of the reduction potentials relative to Li electrode of more than 400 candidate additives

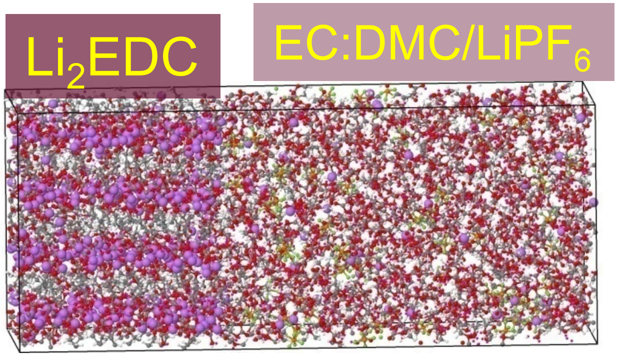




Conductivity of SEI components from MD simulations and experiments (LBL, Phil Ross)



DFT Investigation of Li2CO3growth structures on a graphite edge surface



Properties of the SEI | electrolyte interfacial region

Argonne Nat'l Lab
PI: Amine/Curtiss

Army Research Lab
PI: Borodin

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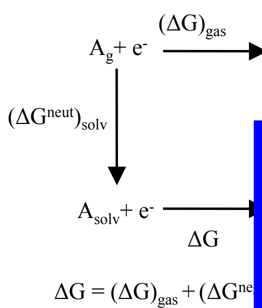
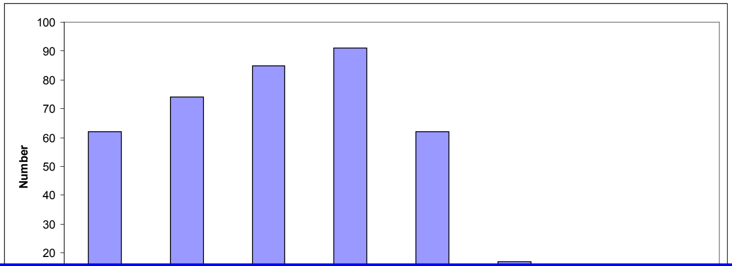
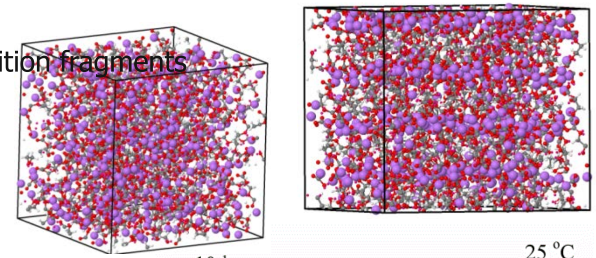
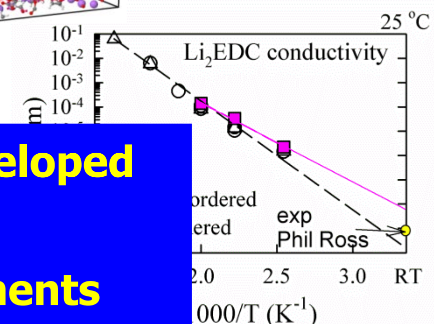






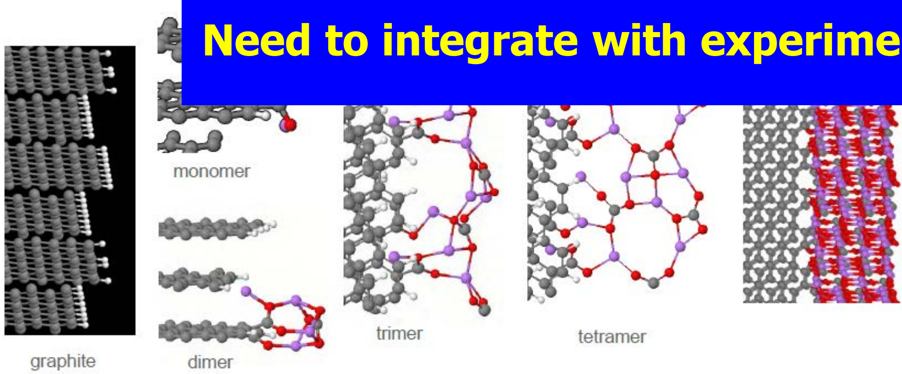


QC/MD computation tools at various levels were developed

Powerful for prediction of SEI formation, transport properties and Redox potential of electrolyte components

Need to integrate with experimental support

ponents from MD
ts (LBL, Phil Ross)



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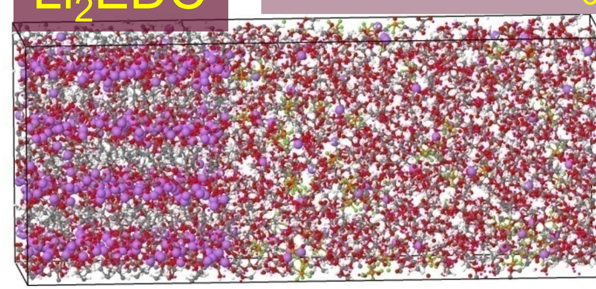
Li_2EDC EC:DMC/$LiPF_6$



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Concluding Remarks

As an indispensable component in LIB, electrolytes dictates the cell performance such as rate capability, high temperature performance and safety.

High voltage electrolyte has made great progress; More efforts are needed to tackle the practical application at extreme conditions.

Non-flammable electrolyte will be another research focus to enhance the cell safety and requires validation in large format cells.

Electrolyte/additive research on high capacity anode (Si, Sn, and alloy) is equally important.

Quantum chemistry simulation will help for the electrolyte design. However, real property still needs to be validated by combining electrochemical testing.